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THE ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN.

BY THEODORE W RICHARDS AND MAX E LEMBERT
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It has been pointed out by many of the workers upon radioactivity, especially by Boltwood, Ramsay, Rutherford and Fajans, that the most conclusive test concerning the recent theory of the degeneration of radioactive elements is to be found in the determination of the atomic weights. If each α-transformation involves the loss of an atom of helium and nothing else which is weighable, the atomic weight of the product should be just 3.99 less than that of the original substance, because 3 99 is the atomic weight of helium evolved during the α-transformation. Thus, if radium has an atomic weight of 225.97,[1] its emanation ("niton") should have an atomic weight of 221.98, radium D (which is supposed to involve three more α-transformations) should be 210.01; and radium G (yet another α-transformation) should be 206.02.

Still more recently, a further theory, which has been independently proposed by Fajans, and by Soddy,[2] indicates that some of the places in the periodic table, corresponding to high atomic weights, should perhaps each include several elements, different in atomic weight but very

...chmid, *Monatsh*, 33, 253 (1912)
...nis, *Ber*, 46, 422 (1913); F. Soddy, *Chem News*, 107, 97(1913); see "The Chemistry of the Radio-Elements," Soddy, II, 3 (1914)

similar in other properties. Thus, in the place which we usually assign to lead, we should expect to find a mixture of ordinary lead, radium B, D and G, and perhaps, also at least one other radioactive product from thorium, and one from actinium. These different substances, according to the hypothesis, should have identical spectra and be inseparable by chemical means, but, coming from different sources, they should have different atomic weights. The theory supposes that each α-transformation involves a loss of valence of two, and each β-transformation a gain of valence of one. The β-transformation involves no change of weight. Thus radium D (supposed to have an atomic weight of 210) after two β- and one α-transformations returns again as radium G to the same place in the periodic system with an atomic weight of only 206. This place is that assigned to lead (which some suppose to be primarily radium G), the only one of the radium series possessed of a long life and not highly radioactive.

The problem is one capable of a decisive gravimetric test; specimens of lead, consisting of different mixtures, obtained from different sources, should have different atomic weights. On the generous suggestion of Dr. Fajans this matter was taken up in the autumn of 1913 at Harvard.[1] In order to glean as much knowledge as was within reach, we have endeavored to obtain as many different samples of radioactive lead as possible and to determine the atomic weights of the possibly composite element by precisely comparable methods, so as to discover if any variation might exist in the chemical equivalents of the different products.

It is a pleasure, at the outset, to express our deep gratitude to many workers in radioactivity who have furnished us with material. Without this general cooperation, it would not have been possible for us to accomplish anything in so short a time, and we cannot express too highly our appreciation.

In brief, the method of analysis was essentially similar to that used so successfully by Baxter and Wilson in their work upon the atomic weight of ordinary lead.[2] The chloride was in each case prepared in a state of great purity by recrystallization in quartz and platinum vessels, after extensive preliminary treatment to eliminate foreign substances. This

[2] Baxter and Wilson, Proc. Am. Acad, 43, 365 (1907).

chloride was carefully dried in a desiccator and heated to fusion in a stream of hydrochloric acid gas and nitrogen, in the quartz tube of the well-known bottling apparatus which has served in so many similar cases.[1] The lead chloride was then dissolved in much water, and the chlorine precipitated by silver nitrate.   Both the weight of silver required and the weight of the precipitate were determined in the usual Harvard fashion.

As a further check upon the work, control analyses giving the atomic weight of ordinary lead were carried out in precisely the same way. These yielded essentially the same value as that found by Baxter and Wilson, and more recently, by Baxter and Grover in work as yet unpublished.

The outcome was striking.   There can be no question that the radioactive samples contain another element having an atomic weight so much lower than that of ordinary lead as to admit of no explanation through analytical error, and yet so nearly like ordinary lead as not to have been separated from it by any of the rather elaborate processes to which we had subjected the various samples.

All the materials used in the work were purified with the care usually employed in work of this kind.   The silver was made by the precipitation of very pure silver nitrate by ammonium formate, and fused upon boats of the purest lime in hydrogen.   The hydrochloric acid gas used for fusion and precipitation was obtained by dropping pure sulfuric acid into chemically pure concentrated hydrochloric acid, furnished by a trustworthy firm and known to be very pure.   It was carefully dried and freed from spray by many towers of glass pearls, drenched with sulfuric acid.   For precipitation this acid was dissolved in pure water in a quartz flask.   The water, and also the nitric acid and other substances used in the work, were purified according to the methods usually employed at Harvard for this purpose.

The description of the preparation of the various samples of lead demands further elaboration.   For the first sample of common lead, used as control material, a commercially pure specimen of non-radioactive lead acetate was three times recrystallized from acetic acid solution and the chloride was precipitated, after considerable dilution, by pure hydrochloric acid gas.   After the chloride had been many times washed and recrystallized from water, its aqueous solution was filtered through a Gooch-Munroe crucible to eliminate threads of filter paper and other solid impurities.   The lead chloride was then twice more recrystallized in a platinum dish and dried over potassium hydroxide (Sample A).

A second sample of ordinary lead chloride was prepared from the purest lead nitrate of commerce in a similar manner.   This salt was crystallized three times in glass and twice in platinum, and its aqueous solution was

precipitated by pure hydrochloric acid gas in a quartz flask. The salt was thoroughly washed with many treatments of wash-water, centrifuged, and finally crystallized three times from a solution weakly acidified with hydrogen chloride in a quartz dish (Sample E).

In order to test the efficiency of crystallization of lead nitrate as a means of freeing this salt from bismuth (the impurity most to be feared in our radioactive material), a sample of this salt was mixed with about one-tenth of its weight of bismuth nitrate. After three recrystallizations only a trace of bismuth remained in the crystals, and the fourth removed all that trace which could be detected by qualitative means. There is no doubt, also, that crystallization of the chloride likewise is a very efficient means of purifying lead.

Our first sample of radioactive lead was very kindly furnished by Dr. Fajans; indeed his generous initiative in this way made it possible for us to begin. It was from Colorado carnotite and came to us as chloride, containing doubtless traces of iron, bismuth, and other substances. It was, in the first place, recrystallized eight times from the aqueous solution, but even after this treatment was not absolutely white in color, containing still a trace of iron. Three more crystallizations from hydrochloric acid solution yielded a product of pure whiteness, but because of the slow elimination of the impurities, this sample, C, could hardly be considered as a final product. Therefore, all the remainder of the material was dissolved in a great volume of water, acidified with nitric acid, and saturated with hydrogen sulfide. The carefully washed sulfide was dissolved in nitric acid, and the nitrate was thrice crystallized (once in platinum) from acid solution. That part of the sulfide oxidized to sulfate was dissolved in ammonium acetate and again precipitated by sulfureted hydrogen, this process being repeated until practically all of the sulfide had been converted into nitrate. The purified and recrystallized nitrate was precipitated as chloride by purified hydrochloric acid gas as before, and the product was recrystallized twice from dilute hydrochloric acid, and once from pure water in a quartz dish (Sample D).

A second source of radioactive lead was very kindly provided by Sir William Ramsay, consisting of residues from pitchblende mined in Cornwall. The brown-gray powder contained ferrous carbonate and many other substances besides lead. This latter element we separated in the first place by the solution of the material in nitric acid, and precipitation with pure sulfuric acid (free from lead) with the addition of alcohol. The sulfate was washed by decantation until practically free from iron, and was dissolved in ammonium acetate and tartrate. That portion of the original residue which refused to dissolve in nitric acid was also treated with ammonium acetate to dissolve any lead which might remain as sulfate. This again was precipitated as sulfide. As before, the sulfide

was converted into the nitrate, and this salt was treated exactly as in the case of Sample D. The resulting product was designated Sample F, and similar material, prepared later from the same substance with somewhat greater care, was designated as Sample G.

A sample of radioactive lead from Ceylonese thorianite, furnished through the great kindness of Professor Boltwood, had already undergone considerable purification. From 25 kg. of the thorianite (which contained about three times as much thorium as uranium), 1100 g. of lead nitrate had been prepared in a state of considerable purity, and 100 g. of this precious material were placed at our disposal. In its preparation, the thorianite had been dissolved in concentrated nitric acid, and the neutralized solution had been precipitated, when moderately dilute, with hydrogen sulfide. The sulfide, after filtration, was then dissolved in hydrochloric acid with the addition of potassium chlorate, and the lead chloride twice recrystallized, converted into nitrate, twice more recrystallized, and came to us at this state. We crystallized it four times more in a quartz dish and finally converted it into the chloride, which was twice recrystallized from acid solution and once from pure water.

A somewhat similar sample, also from Ceylon, came to us through the kindness of Mr. Miner, chief chemist of the Welsbach Light Co., of Gloucester City, N. J., U. S. A. The source was a kilogram of thorianite. This, after solution in dilute nitric acid (the solid residue being separated), was precipitated with oxalic acid to eliminate the thorium, and the filtrate, made alkaline with ammonia, was precipitated with hydrogen sulfide. But much of the lead had gone into the oxalate precipitate, so that Mr. Miner very kindly recovered this also for us, treating the precipitate with sodium hydroxide and extracting with hot water. From this lye, hydrogen sulfide precipitated a mixture of sulfides which contained much more lead. These two samples of sulfides we now united, dissolved in nitric acid and crystallized four times as nitrate. The product was converted in the usual manner into the chloride and designated Sample M. A further product, made from lead oxidized to sulfate by the action of nitric acid, gave another sample N.

When the work was well advanced, a new sample of Bohemian uranium-lead was prepared especially for us through the kindness of Dr. Fajans in the following way: "Das geröstete Erz wurde mit einem Gemenge von H_2SO_4 und HNO_3 (zur Oxydation der vorhandenen Sulfide) behandelt, und dadurch das Uran in Lösung gebracht. Der Rückstand enthielt das Blei als Sulfat, und wurde ihm durch Behandlung mit Aetznatron entzogen, durch Ansäuern wieder ausgefällt, und mittelst Soda in Karbonat verwandelt. Dieses war dann in HNO_3 aufgelöst und das Nitrat kristallisiert worden. Das Präparat wurde unter Ausschluss der Möglichkeit

einer Verunreinigung durch Blei anderer Provenienz gewonnen." This nitrate (which contained lead oxide and traces of iron) was purified in two different ways. One part was precipitated like Sample F twice as sulfide. This was converted into the nitrate, and was three times recrystallized in quartz, being finally turned into the chloride, as usual (Sample I). Another part was recrystallized only three times as nitrate, then turned into chloride, and again recrystallized (Sample K), but according to the results of the analyses it appeared to be as pure as the most carefully treated product. From the lead sulfate which appeared during the solution of the sulfide (Sample I), yet another fraction, L, was made.

Perhaps the most valuable of all our samples (because it came from very pure ore) was a small amount of 3.8 g. of lead chloride very kindly given us by Professor Boltwood and Dr. Ellen Gleditsch, of Christiania, Norway, now collaborating with Professor Boltwood. This product came from the analysis of 110 g. of the purest selected uraninite from North Carolina, U. S. A. The material was practically of pure radioactive origin, no other lead except that from uraninite itself being included. The sulfides, which had been precipitated from an acid solution of the mineral, were dissolved in nitric acid and the lead separated as chloride. This was crystallized three times from hydrochloric acid solution, and, finally, once more from aqueous solution in a quartz dish, and was designated sample O.

Another sample, P, was prepared from the filtrates of all the analyses of Sample D. Silver (in addition to other slightly electropositive elements, if present) was removed by slow fractional electrolysis. The residual electrolyte was repeatedly recrystallized as chloride. It will be noticed that the atomic weight was essentially unchanged.

One of the samples provided by Dr. Fajans came originally from Professor Giesel, and the other had been prepared with a subsidy from the Heidelberger Akademie der Wissenschaften. We wish to express our grateful thanks to these helpers also. A list of the sources of these various samples may facilitate comparison.

Sources of Samples of Lead Chloride.

Sample A. Commercial lead acetate, Germany.
Sample B. Carnotite, Colorado, U. S A (impure) (Fajans)
Sample C. Carnotite, almost pure
Sample D. Carnotite the most carefully purified.
Sample E. Commercial lead nitrate, America
Sample F. Pitchblende, Cornwall, England (Ramsay)
Sample G. Pitchblende, the most carefully purified.
Sample H. Thorianite, Ceylon (Boltwood).
Sample I. Pitchblende, Joachimsthal, Bohemia, purest (Fajans).
Sample K. Pitchblende, preliminary product.
Sample L. Pitchblende, same as I.
Sample M. Thorianite, Ceylon (Miner).

Sample N. Thorianite, later fraction.
Sample O. Uraninite, North Carolina, America (Gleditsch).
Sample P. Extremely careful purification of sample D.
Sample R. Sample O, further purified

The consistent method according to which all these samples were analyzed has already been briefly described but perhaps a few points concerning the details deserve discussion.

The desiccator-dried lead chloride was always fused in a current of hydrochloric acid gas, as already stated, in order to be sure that the water was expelled as completely as possible. There was reason to expect that lead chloride thus fused should be neither basic nor containing an·important amount of dissolved hydrochloric acid. In support of this conclusion we may cite the neutrality of other chlorides thus fused, as determined by the alkalimetric testing of the dissolved material.[1] It is true, of course, that the specific nature of each chloride is different, and reasoning from analogy is not always safe.

After the lead chloride had been cooled within the bottling apparatus in nitrogen, and this gas had been displaced by air, the fused salt in its platinum boat was pushed into a weighing bottle, in which it was weighed with great accuracy. It was then slowly dissolved in a large bulk of warm water (about 40°) contained in a large Erlenmeyer glass-stoppered precipitating flask. We verified the experience of Baxter that no chlorine is lost during this process.

In spite of our precautions, our samples of lead chloride always exhibited on solution in water a small amount (three or four milligrams) of white precipitate, which was shown by its immediate solution in a trace of acid to be a basic salt. This may have been partly due to alkali dissolved from the glass. The literature concerning lead chloride suggested that it may be somewhat hydrolyzed in aqueous solutions.[2] If this is the case, and the trace of basic precipitate came from this cause, it would of course have no effect whatever on the result, provided that it was dissolved in a drop of nitric acid before adding silver nitrate. On the other hand, if the basic salt had been formed during fusion, its presence would signify a real loss of chlorine, and the resulting atomic weight of lead would be too high. We obtained from ordinary lead essentially the same values as those found by Baxter and Wilson (and later by Baxter and Grover); therefore the error (if it exists) must apply equally to both sets of determinations. Because lack of time prevented our solving the question, we strove only for comparative results; our problem was not so much to find the true atomic weight of lead, but rather merely to find if the atomic weight of radioactive lead is like that of ordinary lead. The suitable

[1] See for example Richards and Hönigschmid, THIS JOURNAL, **33**, 28 (1910), *Sitz b Akad Wiss Wien*, 119 (1910); *Chem News*, **104**, 182, 190 (1911).
[2] See for example Abegg's "Handbuch," III, 2nd part, pp. 648–653; also p. 657 (1909)

correction, if any is needed, can be applied at any time, by subtracting a small quantity from each of our values, which were obtained under precisely similar conditions. Professor Baxter and his students have previously met with this difficulty in the cases of both lead chloride and lead bromide and they have been for some time engaged in experiments directed towards solving the problem.

One other correction is involved in three of these analyses, Nos. 21, 25, and 28. In these analyses a combustible black residue, chiefly carbon, of appreciable amount, was left upon dissolving the lead chloride, due doubtless to organic matter taken from the filter paper during purification. In each case this was very carefully filtered off and weighed on a Neubauer crucible, and the weight subtracted from the original weight of lead chloride. These three corrections were, respectively, 0.83, 0.66 and 0.20 milligram. None of the other analyses was entirely free from this carbon-aceous substance, but the amount was in every other case less than the least of those just mentioned and was neglected. Its presence would tend to increase very slightly the observed atomic weight determined from the ratio of lead chloride to silver, but would have no appreciable effect on that referred to silver chloride.

The lead chloride which has been thus weighed and dissolved was pre-cipitated by a weighed amount of silver in the usual way. No unusual precautions were necessary, except that we found that when the solutions were concentrated, lead chloride is more easily occluded by the silver chloride than many other salts.[1] Working, however, with solutions so dilute that only 1 g. of lead chloride was contained in 500 cc. of the solution, we were but little troubled from this source. According to Franke[2] the salt must be about 80% dissociated at this dilution. The precipitate after several days comes to a definite and consistent end point, unchanged by further standing. In order to establish the end point with greater exactness, the solubility of the silver chloride was reduced by cooling the solution almost to 0° before removing the samples to be tested. As usual, silver was added to the very nearly precipitated mixture until 25 cc. portions of the supernatant liquid showed, in the nephelometer, the same cloudiness with excess of added chloride in one test tube as with excess of added silver in the other. The amount of silver exactly equiv-alent to the chlorine having this been found, an excess of dissolved silver was added in order to precipitate the dissolved silver chloride, and the whole was filtered with the usual precautions on a carefully weighed Gooch-Munroe crucible with a mat of platinum sponge. The precipitate was dried to constant weight at about 180°; and then transferred to a porcelain crucible and fused, in order to dislodge the small remaining trace of water.

[1] This confirms the experience of Baxter
[2] See Abegg's Handbook, Loc cit

In the first place, a number of preliminary analyses were made in order to acquire experience in the method. Of course some of them failed for one reason or another, but they yielded important consequences nevertheless. They showed that the method in our hands yielded with common lead essentially the same results as those obtained by Baxter and Wilson— our values averaging about 207.15 for the atomic weight of lead when it did not contain radioactive material. They showed, moreover, that Colorado carnotite contained lead (Samples C, D) having an atomic weight not far from 206.6 by the same method and that the lead extracted from English pitchblende (Sample F) had an atomic weight of about 206.9. The preliminary analyses of the radioactive material need not be recounted in detail because the chloride was not thoroughly purified and the analytical procedure was not wholly without fault. The analyses of common lead may be briefly recounted.

In four closely agreeing analyses, 16.2966 g. of fused lead chloride, after complete solution, required 12.6458 g. of silver for complete precipitation. Thus 100 parts of silver are equivalent to 128.87 parts of lead chloride, and if the atomic weight of silver is taken as 107.88, lead becomes 207.14. Again in two closely agreeing analyses 8.17662 g. of fused lead chloride yielded after due correction, 8.4293 g. of silver chloride. Hence, 100 parts of silver chloride correspond to 97.002 parts of lead chloride, and on the same basis as before, lead becomes 207.16. The mean between these two results, 207.15, may be taken as the experimental value for the atomic weight of ordinary lead as observed under these conditions. This result is about halfway between that found by Baxter and Wilson and that more recently found by Baxter and Grover, but not yet published. Therefore the results indicate that the method had been mastered and that it had been giving sufficiently satisfactory results throughout. The agreement of our results by the two methods shows that no important amount of impurity was occluded by the precipitated silver chloride, in agreement with Baxter's outcome.

Most of the analyses thus summarized were made before the radioactive lead was attacked. In the last one, made at the very end of the work, 5.0089 g. of lead chloride, were fused and dissolved as usual, but before precipitation an amount of the nitrate of radium D (kindly sent by Dr. Fajans) was added, sufficient to make the radioactivity of the mixture correspond approximately to that of Sample D. This was in order to discover whether or not the presence of radioactivity produces serious effect upon precipitation. As the atomic weight calculated from this last result (207.14) was exactly like the average, it is evident that the analytical process is not affected by the mere presence of radioactivity.

Let us now turn to the final results for material obtained from radioactive sources. The work was done with great care, and because of the

experience gained in the preliminary trials, the results were more satis-
factorily concordant. All the figures concerning these final series are
given in the table below, no experiment having been omitted except a single
analysis of Sample O, which was made before it was fully purified, and
was therefore rejected. Table III contains, the weight of silver needed
for each specimen of lead chloride, and Table IV the weight of silver
chloride obtained. The last two columns of each table record, the ratios of

TABLE III.—FINAL RESULTS.

Series 1. 2Ag : PbCl₂.

Number of analysis.	Sample PbCl.	Ag.	Corrected wt. of fused PbCl in vacuum.	Corrected wt. equivalent Ag in vacuum.	Ratio PbCl₂:Ag.	Atomic weight.
16.....	D	X	3,87082	3,00984	1,28606	206,56
18......	D	X ·	5,57331	4,33300	1,28625	206,60
26......	P	Z	5,49412	4,27157	1,28621	206,59
Sum.................			14,93825	11,61441	Av. 1,28618	206,59
17......	H	X	3,88228	3,01600	1,28723	206,81
19......	H	Y	4,05550	3,15061	1,28722	206,81
20......	H	X, Y	4,05168	3,14788	1,28712	206,79
Sum.....			11,98946	9,31449	Av. 1,28719	206,81
24..... ..	M	Y	2,80814	2,18162	1,28718	206,81
21......,.	I	X	3,95052	3,07209	1,28594	206,54
22.......	K	X, Y	2,95726	2,29951	1,28604	206,56
			6,90778	5,37160	Av. 1,28598	206,55
23......	G	Y	4,05702	3,15153	1,28732	206,84
29......	R	Z	2,01795	1,56952	1,28563	206,47

TABLE IV.—FINAL RESULTS.

Series 2. PbCl₂ : 2AgCl.

Number of analysis.	From Series No. 1.	Sample of PbCl₂.	Corrected wt. of fused in vacuum.	Corrected wt. of fused AgCl in vacuum.	Ratio PbCl:AgCl.	Weight Ag = 107,33
40.........	16	D	3,87082	3,99879	0,96799	206,59
42.........	18	D	5,57331	5,75707	0,96808	206,61
50.........	26	P	5,49412	5,67573	0,96800	206,58
Sum.................			14,93825	15,43159 Av.	0,96803	206,59
42......	17	H	3,88228	4,00703	0,96886	206,84
......	20	H	4,05168	4,18265	0,96870	206,78
Sum...............			7,93778	8,18968 Av.	0,96877	206,81
46......	24	M	2,80814	2,89816	0,96894	206,85
45.........	22	K	2,95726	3,05475	0,96809	206,61
47,.........	23	G	4,05702	4,18670	0,96903	206,86
51...........	29	R	2,01795	2,08663	0,96767	206,32

the substances concerned and the atomic weights of lead computed in the usual fashion from these ratios, assuming the atomic weights of silver and chlorine to be 107.880 and 35.458, respectively.

Thus the final analyses yielded results essentially like the preliminary ones. The situation will become clearer if the results are all collected and averaged in a summarized table (V) giving the values of the atomic weight corresponding to each kind of lead.

TABLE V —FINAL VALUES FOUND FOR ATOMIC WEIGHT OF LEAD FROM DIFFERENT SOURCES

Lead from North Carolina uraninite (Sample R)	206 40
Lead from Joachimsthal pitchblende (Sample I, K)	206 57
Lead from Colorado carnotite (Samples D and P)	206 59
Lead from Ceylonese thorianite (Samples H, M)	206 82
Lead from English pitchblende (Sample G)	206 86
Common lead	207 15

The result is amazing. Evidently then the chemical equivalents of these different specimens are markedly different from one another. Because the method of analysis was the same in each case, one cannot help thinking that there is a real variation in the chemical equivalents of these samples of lead. Either a large amount of some element having a chemical equivalent nearly as great as lead, or a small amount of an element having a low chemical equivalent, must be present, mixed with the substance which we ordinarily call lead. The fact that all the analyses were carried out by the same method, and that each sample gives consistent results, seems to exclude the effect of analytical error. The nature of this admixture it would be perhaps premature to decide. Clearly it has reactions very much like those of lead, if not exactly identical; for the various processes to which our material was subjected would have eliminated any element widely different. Moreover, the fact that protracted purification had no effect on the atomic weight of any one sample is evidence in the same direction.

A word should be said concerning the determination of the radioactivity of these various samples, which is an important item in the consideration. The determination was made by means of a quantitative gold-leaf electroscope of the usual type—a square brass box with mica windows, containing a gold-leaf suspended from a flat rod passing through amber. The box was grounded and the electroscope was charged by means of rubbed sealing wax. The material to be investigated was placed on a wooden slide beneath the instrument. The β-rays (which alone were studied) were measured, being allowed to come into the box through a screen of thin tinfoil and aluminum foil. In the first place the time taken for the gold-leaf to fall between two definite points in the micrometer eyepiece of the observing telescope was noticed when no radioactive

*substance was present; then the times for the various portions were
studied under precisely like conditions and compared with the same weight
of uranium trioxide.* From these times of fall the rates were easily com-
puted, and on subtracting from the rates with radioactive substances,
the rate when nothing was present, the comparative values for the various
substances were obtained.   Immediately after purification, of course, the
specimens were practically non-radioactive, because during crystallization
radium E, which is the chief source of the β-rays, goes into the mother
liquor.   As is shown by the figures for our Sample D at the top of Table
VI, the radioactivity of freshly prepared crystals steadily increased in
the usual curve until the maximum was attained in about thirty days
Radium E is then in equilibrium with radium D.   The table gives,
in its lower part, a comparison of the radioactivity of the different samples
It will be seen that Sample D was the most radioactive, sample O next,
and Samples F and G the least   An old sample of uranium trioxide is
included to give an idea of the magnitude of the effect

<div align="center">TABLE VI</div>

Sample of PbCl₂ 1 5 g	Time in days elapsed since crystallisation	Time in seconds of fall of gold leaf with preparation	Rate of fall per minute	Natural fall of leaf per minute	Corrected rate of fall with preparation
D	0 2	472	0 127	0 043	0 084
D	1 2	203	0 296	0 035	0 261
D	2 0	144	0 417	0 035	0 378
D	4 1	91	0 659	0 036	0 623
D	5 2	?78	0 769	0 041	0 728
D	6 1	71	0 845	0 042	0 803
D	7 0	69	0 870	0 043	0 827
D	8 9	64	0 942	0 037	0 905
D	12 1	56	072	0 039	033
D	14 3	53	133	0 043	090
D	16 3	49	220	0 039	188
D	18 0	49	220	0 039	188
D	27 0	43	396	0 046	350
D	40 0	43	396	0 045	1 351
B¹..	>200	47	278	0 031	1 247[1]
1 27 g					
D	59 0	53 0	1 132	0 045	1 087
F	40	265 0	0 226	0 045	0 181
G	24	270 0	0 222	0 045	0 177
H .	35	204 0	0 294	0 045	0 249
I	?	182 5?	0 329?	0 045	0 284?
M	29	257 5	0 234	0 045	0 189
O	20=	85 0	0 707	0 045	0 662
UO₃ standard	>1000	628 0	0 095	0 045	0 050

[1] This sample was taken from the impure original lead chloride from carnotite,
as we had received it   The slightly lower value is probably due to another size of
crystals and the non-radioactive impurities.

Although in general the samples of lead having greater radioactivity' show less atomic weight, the decrease in the atomic weight is not exactly proportional to the radioactivity. For example, preparation O (the same material as preparation R) is distinctly less radioactive than Sample D, although the atomic weight exhibited by O is decidedly more divergent from the usual value than that exhibited by D. The rates of fall for 1.27 g. of O and D, both twenty days old, were respectively 0.66 and 0.99, whereas the deficiencies in the atomic weights of these samples were respectively 0.75 and 0.56. The irregularity suggests the presence of more than two variables. More data are clearly necessary for a definitive conclusion. The attempt to explain the relationship will therefore be deferred.

The spectroscopic examination of one of these samples (Sample D) was conducted with the generous help of Professor Baxter in his admirable Féry quartz spectrograph. Very well-defined photographs of the ultraviolet portion of the spectrum of our Sample D (after it had been recovered from an analysis, and therefore contained a trace of silver) were taken on a film, side by side with similar photographs of Baxter's purest lead. The parallelism of the two, both as regards the number of lines and the intensity of the lines was complete throughout the whole field, from wave length 0.4μ to the extreme ultraviolet visible in this instrument (about 0.200μ) except that the characteristic silver lines 0.3281μ and 0.3383μ were clearly depicted and the prominent copper lines 0.3248μ and 0.3274μ were faintly visible. The latter had an intensity corresponding, on a very conservative estimate, to 1 part of copper in 100,000 parts of lead, determined by comparison with the spectrum of lead containing known traces of copper—an amount far too minute to have any effect on the atomic weight. The silver doubtless came from the analytical operations, as already said; and its manifest appearance is good evidence of the great sensitiveness of the spectrometer. No shifting or obvious broadening of any of the lines was observed, but it would not have been possible to see a very slight effect of this kind.

Thus it appears that the lead from radioactive sources, having an atomic weight of 206.6, gives essentially the same ultraviolet spectrum as ordinary lead, having an atomic weight (determined by the same method in parallel analyses) of 207.15.

The obvious inference to be drawn from this amazing result is that one of four alternatives must hold true. Either the unknown substance, which is mixed with ordinary lead and produces the lower atomic weight, has the same spectrum as lead itself; or else it gives no lines whatever in the ultraviolet range of this photograph; or else the presence of a large bulk of lead hides or aborts the spectrum of the foreign admixture; or else ordinary lead is a similar medley in somewhat different proportions. It is

perhaps premature to decide between these alternatives, but all are of
interest, the first and last of course being the most revolutionary.

That lead should be composed of a mixture of substances of different
origin but similar properties is, after all, possibly not so revolutionary a
proposition as might appear at first sight.   Rare earths are often very sim-
ilar in properties, and large amounts of material and very patient
fractionation are necessary to separate them.   Why should not the same
thing be true of several of the commoner elements?   The only practical
difference besides the presence of radioactivity seems to lie in the fact
that in the present case the intruders produce no obvious change in the
ultraviolet spectrum.   But if all lead is a mixture, this might be expected.

At first sight one might be inclined to feel that the irregularity in the
quantitative results above described should diminish one's respect for the
significance of atomic weights in general, but further thought shows that
this is a superficial view.   If the results which we have obtained really
indicate that several kinds of lead having the same properties and spectrum
may be mixed together and not separated chemically, it is evident that
the atomic weight becomes almost the only criterion, except radioactivity,
capable of detecting the admixture and tracing the factors to their source.
Thus the study of atomic weights is shown to be not less but more signifi-
cant than it had been before.   To emphasize this point, we may perhaps
quote two paragraphs, written seven years ago, long before the theory
under discussion had been proposed, and when such ideas were of a rather
heretical character.   •

"Are the supposed constant magnitudes to be measured in chemistry
really variable   ?   If they are thus variable, is it worth while to
expend much labor in determining the values which they happen to possess
at any one time under any one set of conditions?

"The question as to whether or not the supposed constants of physical
chemistry are really not constants, but are variable within small limits,
is of profound interest and of vital importance to the science of chemistry
and to natural philosophy in general.   If this latter alternative is true,
the circumstances accompanying each possible variation must be de-
termined with the utmost precision in order to detect the ultimate reason
for its existence.   As Democritus said long ago, 'the word chance is only
an expression of human ignorance.'   No student of natural science who
perceives the dominance of law in the physical universe would be willing
to believe that such variations in a fundamental number could be purely
accidental.   Every variation must have a cause, and that cause must be
one of profound effect throughout the physical universe.   Thus the idea
that the supposed constants may possibly be variable, adds to the interest
which one may reasonably take in their accurate determination, and

enlarges the possible field of investigation instead of contracting it."[1]
This matter has received not only speculative but also experimental treatment at Harvard. For many years the possibility that samples of a given element from different sources might have different atomic weights had been considered, and investigated, but never before with a positive outcome. In the first investigation of the atomic weight of copper undertaken by one of us as long ago as 1887,[2] samples of copper obtained from Germany and from Lake Superior were found to give precisely the same atomic weight for this element. More recently the question was revived and in 1897, specimens of calcium carbonate were obtained from Vermont, U. S. A., and from Italy, in order to discover whether or not the calcium in these two widely separated localities had the same atomic weight. Not the slightest difference was found between them.[3] Again, in a very elaborate investigation on the atomic weight of sodium,[4] silver was obtained from several distinct sources and sodium chloride was obtained partly from several different samples of German rock salt, and partly from the salt pumped from the Solvay Process Company's mines at Syracuse, N. Y. These preparations, differing widely in the steps of manufacture and in geographical source, all yielded essentially the same atomic weights within the limit of error of the process.[5] Yet more recently Baxter and Thorvaldson,[6] with the same possibility in mind, determined the atomic weight of extra-terrestrial iron from the Cumpas meteorite, which gave a result identical with ordinary iron within the limit of error of experimentation. From these researches it would seem probable that even if an unusual eccentricity may be exhibited by lead, most elements do not as a rule differ from any such cause of uncertainty. Baxter and Grover are now engaged in the examination of ordinary lead from different geographical sources. Perhaps this also contains more than one component, as suggested above.

It would perhaps be premature to indulge in further hypothetical reasoning concerning the nature of this extraordinary phenomenon, but the nature of the variation unquestionably points in the direction of the hypothesis of Fajans and of Soddy.

This paper must be looked upon only as a preliminary one. More time, larger amounts of material, and more chemical experimentation are needed in order to be sure that the reactions of the unknown contaminating ele-

[1] Richards, (Berlin Inaugural), *Science*, N. S, **26**, 562 (1907); also *Die Umschau*, **13**, 542–543 (1909); translated by F. Haber.

[2] Richards, *Proc. Am. Acad.*, **23**, 179–80 (1887).

[3] Richards, THIS JOURNAL, **24**, 374 (1902).

[4] Richards and Wells, *Carnegie Instit. Wash. Pub.*, **28** (1905)

[5] Even if both specimens of salt came originally from a Silurian ocean, the time and condition of deposition were probably widely different.

[6] THIS JOURNAL, **33**, 337 (1911).

ment and lead are wholly identical. We hope and intend to continue the study, and solve the highly interesting questions which it presents.

We are greatly indebted to the Carnegie Institution of Washington for much of the apparatus and material used in this research.

Summary.

In this paper a description is given of parallel experiments determining the equivalent weights of various samples of lead chloride obtained from different sources. It was found that all of the radioactive specimens possess a lower atomic weight than ordinary lead, as determined under identical conditions, the deficiency in one case amounting to as much as 0.75 of a unit.

No simple linear quantitative relationship between the exact amount of radioactivity and the atomic weight was found. The radioactivity of the various samples was compared by means of the quantitative electroscope.

The ultraviolet spectrum of a typical radioactive sample was compared with that of ordinary lead, with the help of G. P. Baxter, in a quartz spectrograph. No difference was found between the spectra of these specimens, except for a trace of copper too small to affect the result, and a negligible trace of silver known to have been present. The inference seems to be that radioactive lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by chemical means. This substance cannot be identified in the ultraviolet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or aborted by that of lead.

This amazing outcome is contrary to Harvard experience with several other elements, notably copper, silver, iron, sodium, and chlorine, each of which seems to give a constant atomic weight, no matter what the geographical source may have been. No attempt is made here to discuss the theoretical aspects of the facts presented, but attention is called to their qualitative agreement with the hypothesis of Fajans and of Soddy.

CAMBRIDGE, MASS

TWO NEW MODIFICATIONS OF PHOSPHORUS.

BY P W. BRIDGMAN.

The two new modifications of phosphorus to be described here were obtained during an investigation of the effect of high pressure on the melting point of ordinary white phosphorus. The two new forms have perfectly distinct characteristics; in this they are different from the questionable modifications of red phosphorus often announced. The first of these modifications is a new form of white phosphorus, which changes

into the ordinary white modification reversibly under the proper conditions. The second is a form obtained irreversibly from white at high pressures and moderate temperatures, which is 15% more dense than Hittorff's "metallic" red phosphorus.

In addition to a description of some of the physical properties of these two new modifications, this paper will contain an account of a few experiments made on a specimen of red phosphorus formed under somewhat unusual conditions of temperature and pressure; and, at the end will be found a consideration of the problem of the mutual relationships of the various modifications, now at least four in number. No attempt has been made to completely solve the problem, as this is now more properly a research for a chemist than a physicist, and since black phosphorus was discovered only incidentally, in the course of other investigations.

White Phosphorus II.

The new modification of white phosphorus was first produced by increasing pressure on ordinary white phosphorus to about 11000 kg./cm.^{2} at 60°. The existence of the new form was shown by a discontinuous change in the volume at this pressure. A number of points on the transition curve of these two modifications were then obtained at temperatures down to 0°, and the corresponding changes of volume, when one modification passes to the other, were measured. These measurements suffice for a computation of the latent heat and the change of internal energy when the one form passes to the other. These data have already been published,[1] and for convenience of reference the results are reproduced here in Table I.

TABLE I —DATA FOR THE TRANSITION BETWEEN THE TWO FORMS OF WHITE PHOSPHORUS

Pressure. Kgm/cm^2	Temperature.	Δ V. Cm.^{3}/gm.	Latent heat Kgm. m./gm	Change of energy. Kgm. m /gm.
1	—76.9°			
6000	— 2 4	0 00851	18 61	18 10
7000	9 6	825	19 43	18 86
8000	21.4	799	20.24	19 61
9000	32 7	772	21 04	20 34
10000	43.7	746	21 82	21 06
11000	54 4	720	22 58	˙21 77
12000	64.4	694 "	23 29	22 44

The points found at high pressures indicated by extrapolation that there should be a transition point at atmospheric pressure in the neighborhood of —80° C. This transition point at atmospheric pressure has lately been realized.

The method employed was the usual one of determining a heating curve. This method is well adapted to showing the existence of a transition point, but is not capable of giving a very accurate value of the transition

[1] P. W. Bridgman, *Phys. Rev. N. S.*, **3**, 126–141, 153–203 (1914)

temperature, and gives no value for the change of volume. About 100 g.
of white phosphorus were melted under water and allowed to solidify
in a cylindrical mold, in which a platinum resistance thermometer was held
axially. This thermometer had been calibrated between 0° and +60°,
and .the negative readings calculated according to Callendar's formula,
using 1.50 for the value of δ.[1] The maximum error in the temperature
determined in this way cannot be more than 0.1° at —80°. The phos-
phorus with the thermometer was then transferred to a thin metal cylinder
containing pentane, and the whole cooled down·in liquid air. After com-
ing to the temperature of liquid air, the metal cylinder with the phos-
phorus was transferred to a cylindrical Dewar flask, in which it was cen-
trally supported without contact with the walls. The rise of temperature
with time was followed with the platinum' thermometer. Transition
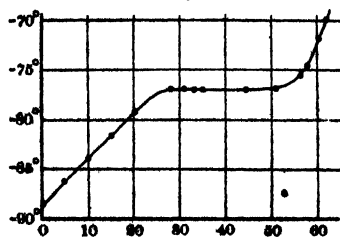from the low temperature to the high temperature modification was shown

by an arrest in the regular rise of tem-
perature with time. This is shown in
Fig. 1. The heat absorbed during the
transformation was sufficient to keep the
temperature nearly constant during half
an hour. There was a very slight retro-
gression of temperature during this half
hour, which shows that there was some
slight superheating before the transition

Fig. 1. Heating curve of ordinary
white phosphorus, temperature in de-
grees against time in minutes. The
arrest point shows the transition from
the low to the high temperature modi-
fication.

started. The temperature found in this
way must, therefore be somewhat higher
than the true temperature of transition.
Just how much higher, it would be im-
possible to say, but the approximate con-
stancy of temperature during the transformation makes it probable that the
temperature found is not far above the true value. This is also strongly indi-
cated by the smoothness of the curve connecting the point at atmospheric
pressure with the points found at the high pressures. The completed
phase diagram of these two modifications is shown in Fig. 2.

In addition to finding the transition temperature at atmospheric pressure,
two attempts were made to determine the crystalline form of the new
modification. The appearance of this new form in bulk is much like that
of ordinary white phosphorus, it may possibly be a trifle yellower, and
there are likely to be cracks formed because of the volume contraction
of about 2% when the transition occurs. In the first attempt to get the
crystalline form, a tube containing white phosphorus was pumped to a
low vacuum and the lower part immersed in a flask with liquid air, while
the upper part containing the phosphorus, was exposed to the tempera-

[1] See Kaye and Laby's tables, p. 46.

ture of the room for 24 hours. It was hoped that the phosphorus would distil from the warm end and condense at the cold end in the character-istic crystalline form of the low temperature modification. The experi-
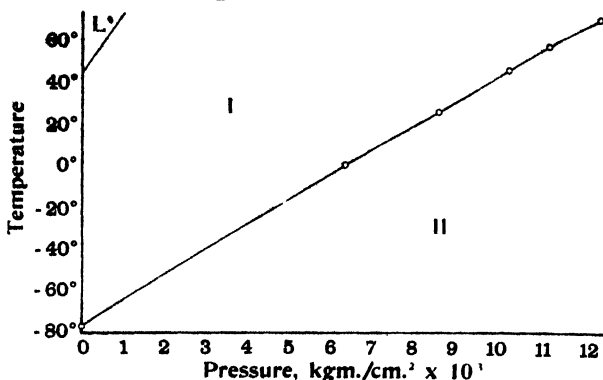

Fig. 2. Shows the relation between temperature and pressure on the transition curve between the two modifications of white phosphorus A short length of the melting curve is shown in the upper left-hand corner

ment failed because most of the phosphorus condensed in the cooler parts of the tube above the part exposed to the liquid air. Only an excessively attenuated mist condensed in the lower part of the tube. With the micro-scope, it was possible to pick out a few needle-like forms, probably the low temperature crystals of phosphorus, but no more exact information as to the crystalline form could be obtained. It should, perhaps, be men-tioned that the crystals were examined at the temperature of the room, so that all that one could expect to see would be crystals of ordinary phosphorus with the outer crystalline form of the low temperature form.

The second attempt to obtain the crystalline form was somewhat more successful. A solution of white phosphorus in carbon disulphide was al-lowed to crystallize at the temperature of a mixture of carbon dioxide snow and gasolene. The phosphorus separates out as a slush composed of fine crystals. Microscopic examination showed that the usual crystalline habit is in needles, about five times as long as broad, with pointed ends of about 60°. It was not possible to specify further the shape of the needles. Scattered among the needles, however, there were occasional plate-like forms of unmistakable hexagonal shape; several nearly perfect hexagons were found. The great probability is, therefore, that this new modi-fication belongs to the hexagonal system. The crystalline form of the usual modification is regular.

A word may be said as to a bearing of this on A. Smit's "New Theory of Allotropy."[1] He found that ordinary liquid white phosphorus behaved

[1] A. Smits and H. L. de Leeuw, Z phys. Chem., 77, 367–379 (1911).

in a way that seemed to suggest that it contained two kinds of mole-
cules; he assumed that the second kind of molecule was the molecule of
red phosphorus. Quite a part from the legitimacy of his experiments, of
which there seems to be some doubt, the hypothesis of the presence of
red phosphorus molecules in appreciable quantity in white phosphorus at
low temperatures is a surprising one, in view of the inappreciable reac-
tion velocity from white to red. The existence of this new modification
of white phosphorus shows that, if the experiments do legitimately point
to the existence of another kind of molecule, it is the molecule of this
new modification, rather than the molecule of red phosphorus.

Black Phosphorus.

Black phosphorus was discovered during an attempt to force ordinary
white phosphorus to change into red phosphorus by the application of
high hydrostatic pressure, at a temperature below that at which the
the transformation runs with appreciable velocity at atmospheric pressure.
The phosphorus used was the purest commercial stick phosphorus from
Eimer and Amend. This had shown itself perfectly free from dissolved
impurities, although it probably contains such impurities as carbon or
water mechanically suspended. The phosphorus was melted under water
into a steel shell about 15 cm. long and 1 5 cm. in diameter, the water
was removed as far as possible, after the phosphorus had solidified, by me-
chanical shaking, and the shell with the phosphorus was placed imme-
diately under kerosene in a high pressure cylinder. Pressure up to about
6000 kg. per sq. cm. was applied at room temperature to the phosphorus
through the medium of the kerosene; the cylinder was raised to 200°
in an oil bath controlled by a thermostat, and the pressure was then
raised to from 12,000 to 13,000 kg. The transition from white to black
phosphorus occurs, under these conditions, in from 5 to 30 minutes. The
pressure drops at first very slowly, then more rapidly until apparently
a critical point is reached somewhere between 11,000 and 12,000, at which
it drops suddenly to about 4,000 kg. Pressure may then be increased
again (with the form of apparatus used this secondary increase could not
be carried beyond 11,000 kg.) with no further drop of pressure. On
cooling the lower cylinder and relieving pressure, the white phosphorus
is found transformed into a black substance of very much smaller volume
than the original white phosphorus. Proof will be given presently that
this is a modification of phosphorus, not a compound. This experiment
has been repeated successfully every time that it has been tried, now five
times in all. About 50 g. of black phosphorus may be formed at a time.

During one of the repetitions of the experiment the effect of inoculating
the white phosphorus with a piece of black phosphorus was tried, with
the idea that under these conditions it might not be necessary to raise
the temperature or pressure so high. It was, nevertheless, necessary to raise

the temperature to 200° and the pressure to 11,750 kg. When pressure and temperature had reached these values, the formation of the black from the inoculated white phosphorus took place in about 5 minutes, a somewhat shorter time than usual. It would appear then, that inoculation may have some effect on hastening the reaction, but the effect is in any event slight, and it may have been due entirely to accidental causes quite apart from the inoculation, judging from the irregularity of the other trials. An attempt to form black phosphorus from white at 175° and nearly 13,000 kg. was without success. Also an attempt to produce black phosphorus from commercial powdered red phosphorus, which had been inoculated with a small piece of black phosphorus was without result in 40 minutes at 12,900 kg. and 200°. Another attempt to produce black phosphorus from the massive red phosphorus, to be described later, was also unsuccessful after 30 minutes at 12,900 kg. and 200°.

The transformation from white to black phosphorus is not quite complete. There is a slight quantity of ordinary red phosphorus formed at the steel walls of the shell or at the surface of contact with the kerosene (never any red phosphorus in the interior of the mass), and throughout the mass of the black phosphorus there may be a few isolated patches in which exceedingly minute traces of white phosphorus remain untransformed. These traces of white phosphorus will catch fire spontaneously on contact with the air, or by friction with the hack saw with which the stick of black phosphorus was cut up for examination. This white phosphorus burns for only a few moments and then goes out, without igniting the mass of black phosphorus.

The black phosphorus presents two distinct characteristic fractures; in some places the fracture is coarsely granular like sugar, apparently crystalline, but the grains under a low power microscope show no semblance of crystalline form, and in other places where the flow under pressure was great, the fracture is fibrous with a metallic lustre, very much like graphite in appearance. In spite of the high pressure of formation, the mass of the black phosphorus is permeated with pores, some of which may be several millimeters in diameter. These pores may at first be filled with kerosene. The presence of these pores doubtless accounts for the slight apparent increase in weight of the specimen after the transformation. In the endeavor to show that the new substance was really a new modification of phosphorus, and not a chemical compound with kerosene or iron, the total weight of two samples was measured before and after the transformation. After formation, the samples were dried by mechanically shaking the kerosene from the surface. The gain of weight of each of the samples was about 2%; too small a gain to be accounted for by the formation of a chemical compound, and sufficiently explained by the

presence of kerosene in the pores. The presence of such occluded kerosene was evident to the sense of smell.

In order to make the proof still stronger that the substance formed was really a new modification of phosphorus and not a compound, C. T. Hawkins very kindly made an analysis of two samples at the Chemical Laboratory of Harvard University under the direction of G. P. Baxter. These samples had been broken into pieces about the size of a pea and soaked in carbon bisulphide to dissolve the white phosphorus, but had not otherwise been purified, as by exhausting in vacuum, for example. The sense of smell showed some kerosene still present. The results of the analysis are as follows·

Wt of black phosphorus	Wt. of $Mg_2P_2O_7$	Per cent. phosphorus
0 1622	0 5669	97 5
0 1754	0 6182	98 3

The first sample was treated by dissolving in concentrated nitric acid and the second in fuming nitric acid. Preliminary attempts to dissolve the phosphorus in dilute nitric acid showed that under these conditions a large part of the phosphorus was lost as volatile matter during dissolution. The amount of carbon present in the sample was 0 4% or more. No attempt was made to analyze the other 1 5% of impurity, which, in all probability, was water or kerosene. A measurement, to be given later, of the magnetic properties, shows no trace of iron. The fact that the total impurity is less than 2%, and that at least some of this impurity is accounted for, makes it absolutely certain that we have here another modification of phosphorus and not a chemical compound.

The most striking difference between the new black phosphorus and previously known modifications is its high density. The density of ordinary solid white phosphorus is 1.83, and that of red phosphorus may vary according to the method of preparation from 2 05 to a maximum of 2.34 for Hittorf's "metallic" crystallized red phosphorus. Nine determinations of the density of different specimens of black phosphorus were made; several of these were determinations of fairly large pieces by weighing under water, and several were determinations by the suspension method, using a mixture of bromoform and carbon tetrachloride. The density of the large pieces varied widely because of the effect of pores; the minimum density found by weighing in water was 2.47 and the maximum was 2.654. The suspension method, of course, gives more accurate results. The specimens measured by this method had been ground in a glass mortar and purified by soaking in several changes of carbon disulphide for several days, exhausted in vacuum at 100°, boiled in four or five changes of distilled water for eight hours, and exhausted in vacuum at 140° for several hours. Furthermore, the air was exhausted from the pores while the phosphorus was in the suspending liquid. Two different

specimens prepared by this method gave absolutely concordant results for the density, 2.691 at room temperature. The minimum density found by the suspension method for larger pieces less carefully purified was 2.66. We accordingly accept the value 2.691 as the true density of black phosphorus, a value 15% higher than that of the most dense variety of red phosphorus. The conclusion is inescapable that this is a new modification of phosphorus, quite distinct from red phosphorus and, because of its higher density, presumably a more stable form.

Black phosphorus does not catch fire spontaneously, can be ignited with difficulty with a match, and may be heated to perhaps 400° in the air without spontaneous ignition. Unlike commercial red phosphorus, it cannot be ignited by striking with a hammer on an anvil. It is almost, if not entirely, stable in the air. It was discovered in the summer time; pieces of the unpurified phosphorus which had remained for several months freely exposed to the air of the room were observed to collect a thin film of moisture, probably phosphoric acid, as red phosphorus is known to do. But several purified specimens, left for six months exposed to the air of the room during the cold half of the year, have collected no moisture whatever. It may be that the difference was due to the difference in atmospheric conditions at different times of the year, but more likely the effect was due to impurity, and pure black phosphorus is absolutely stable in air. A few simple tests seemed to show that it is much like red phosphorus in chemical properties; it is attacked by cold nitric acid, is not acted on appreciably by sulfuric acid, and is not dissolved by carbon disulfide.

When black phosphorus is heated in a closed glass tube it vaporizes and condenses in the colder parts of the tube to red and white phosphorus. The appearance under these conditions is exactly the same as when red phosphorus is similarly treated. It would seem, therefore, that the vapors of black and red phosphorus are, at least in large part, identical. The vaporization from black phosphorus is slow, as it is also from red phosphorus. If distillation from the hot to the cold parts of the tube is pushed to completion by heating for several hours, the black phosphorus leaves behind it a very fine, feathery, black residue, which is unaltered by further heating the glass to redness. This residue is in all probability the slight impurity of carbon disclosed by the above analysis.

Professor Palache of the University Museum, was kind enough to determine the mechanical hardness of black phosphorus and to make a microscopic examination for the crystalline form. The hardness is about 2. Under the microscope none of the ground fragments show any semblance of external crystalline form. The fragments are opaque, except the most minute, which are translucent of an olive-brown color. These very minute fragments between crossed nicols show extinction and illumination with slight changes of color in perpendicular directions.

Black phosphorus is, therefore, unmistakably crystalline, and the crystal system is not regular; the fragments are too minute to permit any further specification of the system. That the crystalline structure should be very minute is what one would expect from the rapidity of formation and the great distortion during formation under high pressure; in fact it is rather surprising that there should be any crystalline structure on a scale large enough for microscopic detection.

The specific heat of black phosphorus was determined by the method of mixtures, using about 40 g. of the ground and purified substance. Several preliminary determinations gave results near those finally obtained, but the proportions of the apparatus were not good. Two final determinations with improved apparatus gave 0.1716 and 0.1685, mean 0.170 g. cal. per g., as the average specific heat at constant pressure over the range from 30° to 100°. One of the reasons for making the specific heat determination was that it might give an idea as to the relative stability of black and red phosphorus. Analogy with other substances would lead us to expect that the more stable form would have the lower specific heat. The specific heat of red phosphorus between 15° and 98° has been found to be 0.170 by Regnault, and Wigand has found 0.183 for the range 0° to 51°, and 0.212 from 0° to 134°. The agreement between these values for red phosphorus is not good, due in part to the different sources of the material, but there can be little doubt that the correct value is above 0.170. It is unfortunate that Hittorf's "metallic" red phosphorus cannot be obtained in sufficient quantities for a determination of its specific heat, because this is apparently the only variety of red phosphorus with definite properties. The evidence afforded by the specific heats is not very valuable, therefore, but such as it is would indicate that black phosphorus is a form of greater stability (greater entropy content) than red phosphorus.

Black phosphorus is a fairly good conductor of electricity, in distinction from white and red phosphorus, which in the pure state seem to be nearly perfect insulators. It is usually stated in tables that white phosphorus is a perfect insulator, but that red phosphorus has some conducting power. This is on the authority of Faraday. The conductivity of red phosphorus found by Faraday must have been due to some slight impurity, however, because very recently Stock and Stamm[1] have found that the most carefully purified Hittorff's red phosphorus is a perfect insulator, and is therefore not at all entitled to its usual appellation of "metallic." The specimen of black phosphorus whose conductivity was measured here was selected from all the available pieces for its great apparent compactness. It was prepared by turning in a lathe, leaving for the final test a cylindrical piece about 1.52 cm. in diameter and 2.69 cm. long. The

[1] A. Stock and E. Stamm, Ber., 36, 3497–3513 (1913).

electrodes were attached by copper plating terminals on the plane ends and soldering copper wires to the copper plating. It is possible in this way to make somewhat better contact than by using a contact with mercury, even when the surfaces are freshly scraped under mercury. The temperature coefficient of resistance was found between 0° and 75° in an oil bath with thermostat regulation. There may be some slight error introduced by imperfect contact at the copper plating; the plating is not firmly adherent as to a metal surface, but may be pulled off with the fingers. However, this error can be only slight, as is shown by the nearly perfect return of the resistance to its zero reading after raising the temperature to 75°. The character of the conduction is entirely metallic; there is not the slightest polarization effect on closing or opening the circuit. Measurements of the resistance were made on a Carey Foster bridge, using a current through the phosphorus not greater than 0.2 amp. The value found for the specific resistance is 0.711 ohms per cm. cube at

0°. The temperature coefficient of resistance has a large negative value, and between 0° and 75° the relation between temperature and resistance is nearly linear. Fig. 3 shows the relation between temperature and resistance over this range. It is evident that presently, at some higher temperature, the curve must depart from linearity. The temperature coefficient of resistance at 0°
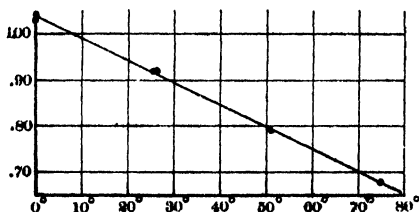

Fig. 3.—The resistance in ohms of a cylinder of black phosphorus as a function of temperature. Notice that the resistance decreases rapidly with increasing temperature.

is —0.00465; this is an unusually high value, higher than for any substance usually listed. It is about 10 times higher than for carbon, and makes it practically certain that the small amount of carbon known to be present cannot be taking a large share in the conduction. It should be remarked that in respect to the sign of the temperature coefficient black phosphorus is not like the metals. The specimen of black phosphorus whose resistance was measured contained, like all large pieces, a number of fine pores, as is shown by the low value of its density, 2.562. About 5% of the total volume must have been occupied by pores, therefore. Precisely what effect these pores would have on the value of the specific resistance is uncertain, because the shape of the pores makes a difference, but in any event the specific resistance of pure black phosphorus must be somewhat lower than that given above.

It may pay to pause here to take thought of this conductivity of black phosphorus. Here is a substance which in two modifications possess no electrical conductivity, but in some way, when the atoms are rear-

ranged more closely together, sets free electrons and becomes a conductor." It would seem to point to some more deep-seated change than a mere rearrangement of atoms; possibly the electrons are squeezed out of the atoms by their great propinquity. Phosphorus is not the only example of this; graphite and carbon are another case in which the volume relations of phosphorus are reversed. But in any event, this is a significant fact for contemplation.

As we might expect from its electrical conductivity, black phosphorus is also a rather good conductor of heat. Observations of the thermal conductivity were of the roughest qualitative nature; when soldering the leads to the copper plated terminals the entire mass of phosphorus rapidly became too hot to hold in the hand, very much more rapidly than would a piece of glass, for example.

The magnetic permeability of black phosphorus was very kindly determined in the laboratory by H. C. Hayes. It is feebly diamagnetic; less diamagnetic than either red or white phosphorus. He found for two specimens the values $-0\ 27$ and $-0\ 29 \times 10^{-6}$. This diamagnetism makes it evident that any impurity of iron can be present only in excessively minute quantities.

The Relation of the Several Modifications.

The most important problem connected with this new modification is the determination of its relation to the other known modifications of phosphorus. It was hoped that the existence of this new modification might offer some clue to the vexed question as to the true nature of red phosphorus. Some facts of importance have been found, but the exact nature of the relationship has not yet been discovered. In the course of the investigation red phosphorus was prepared in a somewhat unusual way, and was found to have slightly different properties from the usual varieties. The rest of this paper will contain a description of this new red phosphorus and of the experiments to determine the relation of the different modifications to each other.

It seemed reasonable to expect that black phosphorus might be prepared by the application of pressures lower than 12,000 kg. at temperatures considerably higher than 200°. It is surprising that no experiments seem ever to have been made on phosphorus at high temperatures at pressures higher than its own vapor pressure. A long steel cylinder, about $^3/_4$ inch in inside diameter, was made for the attempt at higher temperatures. The lower end of the cylinder, which was to contain the phosphorus and was to dip unto a bath of molten lead, was closed by a packing device of copper rings, much like the packing recently described.[1] The upper end of the cylinder projected far enough beyond the lead bath so that it could be kept cool with water, and connection was made at this end

[1] P W Bridgman, *Proc Am Acad*, 49, 627-643 (1914)

with a Cailletet pump giving 1000 kg. In the first experiment, commer-
cial red phosphorus powder was placed in a trap with a seal of fusible
solder containing 50% bismuth in the lower part of the cylinder, and ex-
posed to a dull red heat at 400 kg. for 30 minutes. On cooling and re-
leasing pressure, the red phosphorus was found completely permeating
the solder. The appearance was that of a solidified emulsion. Evi-
dently at the high temperature the red phosphorus had dissolved in the
solder and separated out on cooling. If any of the crystallized Hittorf's
phosphorus was formed, it must have been in very small quantity, al-
though a fairly large yield might be expected under the conditions of high
pressure. In a second experiment, in order to avoid the solvent action
of the solder at the high temperatures, pressure was transmitted directly
to a specimen of red phosphorus by a heavy tempering oil. This was
heated and pressure applied as in the first experiment. The white phos-
phorus changed to red almost immediately, judging by the sudden drop
of pressure, but there was no further change The cylinder was found
filled with red phosphorus and the soft charred residue of the tempering
oil. In a third attempt, ordinary white phosphorus was placed under
water, and heated as before to a dull red, pressure being transmitted by
the water. In this run, pressure was kept at 850 kg. for 6 hrs., then raised
to 950 kg. for 1³/₄ hrs., and then raised to a maximum, 1000, for 10 or 15
minutes. After this time at the maximum pressure, a slight leak developed
owing to the stretching of the steel. The cylinder was immediately re-
moved from the lead bath and plunged into cold water The white phos-
phorus was found entirely transformed into a bright brick-red variety,
compact, and with no evident trace of white phosphorus. This is what
one would expect from the high pressure of formation; during the cooling
there was no chance for any of the red phosphorus to vaporize and con-
dense as white. The red phosphorus prepared in this way shows in
general a bright red fracture, but when scratched with a knife or a piece
of glass shows a gray metallic streak. Furthermore, there are isolated
patches throughout the mass where the fracture shows black, as if the trans-
formation to black had begun here. The density of fairly large pieces
of the red phosphorus is 2.26, but the density of the smallest heaviest
pieces (these heaviest pieces were bright red in color) was found by the
suspension method to be 2.387, a value higher than for Hittorf's "metal-
lic" phosphorus (2.34) or even for the "phosphore pyromorphique" of
Jolibois[1] (2.37), about which there seems to be some doubt.

This red phosphorus was purified by the same method as the black
phosphorus, although no impurity could be detected in it. When heated
in a closed tube it vaporizes and condenses to red and white phosphorus

[1] P. Jolibois, Compt. rend., 149, 287–289 (1909); 151, 382–384 (1910).

... may not the ordinary commercial red phosphorus. The bright red phosphorus ... ...

Red phosphorus of the same bright red color may be prepared by heating commercial red phosphorus under its own vapor pressure to a high temperature (almost a yellow) in a heavy nickel steel bomb. This bright red preparation shows the same gray metallic streak when scratched as that prepared at a higher pressure and lower temperature. It is barely possible that the bright red color of these two preparations is due to a minute impurity of iron, since both of these specimens were directly in contact with the steel walls of the cylinder. Red phosphorus heated under its own vapor pressure in a glass vessel to a lower temperature does not assume this bright red color. However, the iron present must be very minute in quantity, because the bright red phosphorus can be evaporated without sensible residue.

Apparently, the physical information most important for a determination of the relation of red and black phosphorus is a knowledge of the vapor pressures. The best way to measure the vapor pressure would be by use of a quartz membrane, but in the absence of the proper apparatus, two attempts were made with other methods. The first was by a method due to Hittorf,[1] and apparently not used since. The phosphorus under investigation is placed in the sealed short arm of a U-tube, which is closed below by a column of molten metal, as bismuth or lead, which exerts no appreciable vapor pressure at the temperature in question, as would mercury. The free surface of the metal in the long arm of the U is acted on by gas pressure, which may be measured at room temperature with an ordinary mercurial manometer. This original design of Hittorf's was so modified as to give the difference of vapor pressure of the two modifications, by putting red phosphorus in the one arm and black phosphorus in the other arm of the sealed U and observing the difference of level of the columns of melted metal on the two sides. The first measurement at the temperature of the vapor of boiling sulfur showed a greater vapor pressure over the red phosphorus by at least 7 and cm. of mercury. But later attempts with a modified apparatus to get the vapor pressure of the two modifications separately gave values much too high. There must be some chemical action between the phosphorus and the molten solder. Hittorf found the same thing, although his results, using bismuth instead of a solder of tin and lead, were too low rather than too high. In any event, there is apparently no metal melting within the proper range that is without chemical action, and this attractively simple method had to be abandoned.

The method finally used is also one originally due to Hittorf. A small piece of phosphorus is enclosed in an evacuated tube of known volume and

[1] W. Hittorf, Pogg. Ann., 126, 193–228 (1865).

heated to the desired temperature. After heating long enough to make sure that the vapor has reached its maximum pressure, the tube is removed from the bath and allowed to cool quickly at the temperature of the room. The phosphorus vapor condenses on the sides of the tube as white phosphorus, and its amount may be determined either by dissolving it in CS_2, as did Hittorf, or probably with greater accuracy by determining the loss of weight of the original specimen. The vapor pressure is then computed, assuming that the molecule of phosphorus vapor is 4-atomic. This value of the molecular weight seems to be established beyond doubt for the temperature range used here.[1]

Determinations of the vapor pressure of red and black phosphorus were made in this way at the temperatures of boiling mercury and sulfur. It is essential that the temperature of the tube be constant, as is ensured by a vapor bath, or else there will be a continued distillation from the hotter parts to the cooler parts with condensation in the form of red phosphorus, giving too high a computed vapor pressure. The temperature was sufficiently uniform during these experiments, for no condensed red phosphorus was found. Care was taken to avoid any possible distillation during warming to the temperature of the bath by placing the tube suddenly in the vapor after boiling had been going on for some time.

TABLE II.—VAPOR PRESSURE OF PHOSPHORUS IN CM. OF MERCURY.

Temperature. °C.	P. W. Bridgman.		W. Hittorf.		L. Troost and P. Hautefeuille.	
	Black phos.	Dense red phos.	Ordinary red.	Crystallised red	White	Ordinary red.
357.1°	2.3	5.2	..			
358	..	..	3.15			
360	..	..	..		245 0	9 1
400	..	..	37.1	...	..	..
440	..	..	..	..	570 0	133.0
443.7°	..	73.2	..			..
	58.5		..			
	..	..	164 0	93 0		
	..	..		..		517.0
490			..		1370 0	
502			..	..	1660 0	
510	..		..		..	820.0
511	..				1990 0	
530	..	..	614.0	413 0		
550	..	..	..	..	..	2360 0
577	..	..	...	..	..	4260 0

The results are shown in Table II, together with those of previous observers. The agreement of the previous results is not good, but in general the conclusion is justified that the vapor pressure of black phosphorus

[1] A. Stock, G. E. Gibson and E. Stamm, Ber., 45, 3527–3539 (1912).

the black phosphorus is found solidified to a glassy mass, of density 2.18, of a definite brown color, identical in appearance with that obtained when red phosphorus is similarly treated. In fact, there is no reason to suppose that the melts of black and red phosphorus are not identical. The minimum pressure of the nitrogen during this run was 150 kg., and it was increased slowly during the heating to a maximum of 400 kg. After the run, the glass capsule was found to have been expanded by the vapor pressure within, in fact, expanded with enough force to stretch a thin steel shell which contained it. The pressure of the vapor must, therefore, be considerably above 150 kg., and is probably in the neighborhood of 300 kg. at a bright red. In a second experiment, red and black phosphorus were placed together in the capsule and heated for about 20 minutes to 630°. The temperature was read with a pyrometer, but there is possibility of error in the exact temperature. The red phosphorus (this was the bright red phosphorus formed as mentioned above at a dull red at 900 kg.) had partially melted and solidified to a chocolate-brown mass. The black phosphorus showed no signs whatever of melting, but had lost its bright metallic luster. There was no trace of condensation of the vapor of the red on the surface of the black. The external pressure in the nitrogen was kept constant for this experiment at 150 kg. The melting point of black phosphorus is therefore probably somewhat higher than that of red. A third experiment was made in the endeavor to heat the phosphorus hot enough to melt the red but not hot enough to melt the black. If the red and the black stand to each other in the relation of unstable and stable solids of the same liquid, then it might be expected that the entire mass of the red would be transformed into black through the liquid. The experiment was unsuccessful, however; both black and red had melted together to the same glassy mass. Evidently, if this experiment is to be successfully performed, the temperature must be capable of more accurate adjustment than was possible with the crude means at hand.

Two experiments made at high pressures may be mentioned also as possibly throwing some light on the problem. The first was an attempt made before the existence of black phosphorus was known. White phosphorus was compressed to 30,000 kg. at room temperature for 15 hours without result. One would almost expect that black phosphorus would have been formed at this high pressure. The second experiment was made unintentionally while determining the freezing curve of ordinary white phosphorus. Successful measurements of the freezing pressure had been made up to 150°, and a run had been begun at 175° with every prospect of success, when the character of the melting changed suddenly from that of a pure liquid to that of a liquid with a dissolved impurity. There was a pronounced rounding of the corners of the curve giving the change of

volume as a function of pressure. The impurity did not increase with time, but stayed constant after it had once formed. This was shown by the fact that the melting curve could be retraced. On examining the phosphorus after the run, it was found of a bright orange color. The effect was in all probability due to the formation of a slight quantity of red phosphorus at the high pressure (5000 kg.) and temperature, which then dissolved in the white phosphorus. It has been many times suggested that the varieties of red phosphorus formed at low temperatures, as Schenck's, for example, are really solutions of one modification in the other, but this is apparently the first direct proof that such a combination of the two varieties really has the properties of a true solution, giving a depressed freezing point. The effect was not found on repeating the experiment, but sharp melting curves were found up to 200°. If the effect were due to dissolved kerosene, it would have been found on repeating the experiment. Probably some small accidental impurity acted as a catalyzer during the first run. It is well known that there are a number of catalyzers for the reaction from white to red phosphorus at low temperatures.

Finally, in the light of these experiments, some speculation may be allowed as to the probable nature of the phosphorus modifications. The problem of white phosphorus II need not concern us here, for this changes into I by a reversible process, and presents no greater difficulties (which are nevertheless great enough) than any polymorphic transformation. The problem of the nature of red phosphorus has chiefly engaged attention hitherto. The most striking fact is that the density of red phosphorus varies according to the temperature of formation. With the exception of Hittorf's crystallized variety, it is obvious that red phosphorus is not a single well defined substance. This has led Cohen and Olie[1] to suggest that ordinary red phosphorus is a mixture of white and Hittorf's phosphorus in dynamic equilibrium, the equilibrium ratio of the two components changing with temperature. The objection to this is that a dense phosphorus formed at a high temperature does not assume the appropriate lower density when maintained indefinitely at a lower temperature. The explanation suggested by the above experiments is that red phosphorus is a transformation product from white phosphorus to something else, in which the transformation has not run to completion, but is prevented by friction. The distinction between frictional and viscous resistance should be kept in mind; viscous resistance gradually decreases with time, but a true frictional resistance never falls below a certain limiting value. That there should be a true frictional resistance to the reaction from one solid to another is not surprising, and is, moreover, something which has been most strongly suggested by other experiments

[1] E. Cohen and J. Olie, Z. phys. Chem., 71, 1–27 (1910).

on polymorphic transformations between solids at high pressures." I hope
to make this the subject of a special paper.

That there is a frictional resistance is also consistent with the remarkable
manner of change of white to red phosphorus. If the change from white
to red took place by the growth of a surface of separation with a definite
velocity, as during the formation of many crystals, then the hypothesis
of an incomplete transition would not be tenable. But apparently the
change from white to red does not take place in this manner; it has been
carefully observed microscopically a number of times,[1] and nothing of
the nature of the growth of a surface of separation has ever been detected.
The method of transition seems rather to be by the formation of micro-
scopic or sub-microscopic nuclei, which do not grow appreciably in size,
although some sort of change whose nature has not been determined does
go on within the nuclei. More complete transition from white to red
phosphorus means the existence of a greater number of nuclei, not an in-
crease in size of the individuals. If the mechanism of transition is by the
formation of nuclei, which do not grow, it is at least conceivable that
there should be a frictional resistance as the space occupied by the nuclei
becomes greater and they come to interfere more and more with each
other. The effect of increasing temperature is to decrease the frictional
resistance to transformation so that the reaction can proceed further.

The existence of a frictional resistance to transformation makes under-
standable the different densities of red phosphorus formed at different
temperatures, it shows why we are not to expect a reverse change of den-
sity on cooling to a lower temperature, it explains why the solution of red
phosphorus in white at the freezing determination at 5000 kg. and the low
temperature of 175° was so dilute and did not grow in strength, and it
explains why red phosphorus does not show a sharp melting point as would
be expected if it were a single pure substance, but instead melts over an
interval like a solution.[2]

The transformation, of which red phosphorus is a part way product,
may well be a combination of two simpler transformations. It seems very
reasonable to suppose that the suggestion of Wahl[3] is valid; namely, that
in ordinary red phosphorus we have a mixture of amorphous glassy red
phosphorus with crystalline grains. The crystallization of the glass is
prevented by friction, and as the temperature rises, a larger part of the
glass crystallizes, so that the density is higher as the temperature of forma-
tion is higher. But it is questionable whether all the change of density
can be explained in this way; Schenck's red phosphorus has a density
of 2.05, whereas a glass formed in an experiment above by rapid cooling

[1] R. Nedenstam, Diss., 42, 692-694 (1910).
[2] A. Stock and H. Stamm, Loc. cit.
[3] W. A. Wahl, Öfv. Fin. Vet. Soc. Förh., 54, No 9 (1911-1912).

has a density of 2.18. It is very probable that in addition to the effect of Wahl, we must regard the glass itself as in a varying state of transformation.

The problem of the phenomena of vaporization is a complicated one, and one which we do not particularly need to consider in this connection. It has been suggested that we probably have to do here with an irreversible reaction in the vapor phase.

With regard to the relation between black and red phosphorus we can offer only conjectures. It does seem pretty certain, however, that red and black cannot stand in the relation of ordinary monotropic solids. If they did bear this relation, the black must be the more stable form, because of its lower vapor pressure, and in this case we cannot understand the failure of the red to condense as black out of its vapor. The fact that the black apparently melts to the same liquid as the red is puzzling. It may be that the relations here are the same as in the vapor phase; that is, liquid black phosphorus may be unstable, and may transform itself irreversibly to liquid red as rapidly as it is formed.

Summary.

Two new modifications of phosphorus have been found. The first is a new modification of ordinary white phosphorus, possibly hexagonal, with a reversible transition point at atmospheric pressure at about $-76.9°$. The second modification, black phosphorus, is obtained irreversibly from white phosphorus at 12,000 kg. and 200°. A number of its physical constants have been determined; particularly striking are its high density, 2.691, and fair electrical conductivity. No attempt to transform either white or red to black phosphorus has been successful by any other method except that above. Finally, some conjectural explanations of the relations of the various modifications have been given.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY; CAMBRIDGE, MASS

THE DISSOCIATION PRESSURES OF AMMONIUM- AND TETRAMETHYLAMMONIUM HALIDES AND OF PHOSPHONIUM IODIDE AND PHOSPHORUS PENTACHLORIDE.

BY ALEXANDER SMITH AND ROBERT PRYTON CALVERT.
Received May 8, 1914.

The dissociation pressures of the chloride, bromide, and iodide of ammonium and of phosphonium iodide have previously been measured. The methods used, and the results obtained are discussed below. The dissociation pressures of the chloride and iodide of tetramethylammonium,

and of phosphorus pentachloride have not previously been determined. The present observations were made partly to supply data required for a study of the density and degrees of dissociation of the saturated vapors of these substances, in regard to which no previous measurements have been made.

The advantages and disadvantages of the various methods of measuring vapor or dissociation pressures have been considered critically by Smith and Menzies.[1] The method of confinement over mercury, in particular, is not applicable when, as in the present work, chemical action with the mercury occurs. In such cases, various dynamic methods have been employed. The most popular of these, Ramsay and Young's dynamic method,[2] however, presents especially grave irregularities when applied to cases of dissociating solids, in five of which, for example, the temperature of volatilization appeared to be independent of the pressure.[3]

The dissociation pressure of a solid may be measured by means of the spiral manometer of Ladenburg and Lehmann[4] or the dynamic[5] and static[6] isoteniscopes of Smith and Menzies. In the former method, as Smith and Menzies pointed out,[7] permanent distortion of the spiral may occur. Then too, the expansion of the glass makes the zero point change with the temperature, so that the trustworthiness of the measurements is considerably diminished unless the spiral is calibrated for each temperature.[8] The method of Smith and Menzies has been used successfully in difficult cases by Ruff,[9] Taylor and Hulett,[10] and Moles.[11]

The Apparatus.

The isoteniscope used in all our work, except that dealing with phosphorus pentachloride, was the *static*. The substance, the vapor or dissociation pressure of which is to be determined, is placed in the small bulb shown on the right (Fig. 1). The bend is filled with some substance which, at the temperature of the experiment, will melt to give a liquid suitable for confining the vapor. The isoteniscope is connected with a very large bottle for regulating the pressure. By the turning of the proper stopcock, this bottle can be put into communication, either with a similar vacuum bottle, with a compression pump (or the atmosphere), or with

[1] "Studies in Vapor Pressure, III," THIS JOURNAL, 32, 1412 (1910).
[2] J. Chem. Soc., 47, 42; Ostwald-Luther, [3] 218.
[4] Phil. Trans., 177, 116 (1886).
[5] Ber. physik. Ges., 4, 20 (1906).
[6] THIS JOURNAL, 32, 1448 (1910)
[7] Ibid., 32, 1419 (1910).
[8] Ibid., 32, 1455 (1910).
[9] Bremer and Brockmüller, Z. physik. Chem., 81, 196.
[10] Z. anorg. Chem., 72, 63.
[11] J. phys. Chem., 17, 565.
[12] An. Soc. España. de Fis. y Quím., 9, 260 and 272.

the pressure gage. To make a determination of the vapor pressure, the isoteniscope is placed in a well stirred bath, maintained at the proper temperature, and the pressure is lowered until the substance in the bulb boils vigorously. Adhering air, moisture, and volatile impurities are thus carried out past the liquid seal in the bend. The pressure is then raised until the boiling stops and the level of the confining liquid becomes the same in both arms of the isoteniscope. The temperature of the bath and the pressure in the apparatus are then noted and recorded.

The **pressure gage,** a portion of which is shown in Fig. 2, was of the closed mercury-manometer type.[1] Each arm had a length of 2500 mm. and an internal diameter of 16 mm. The scale was engraved on silver inlaid in a heavy steel bar. It was graduated in mm. and calibrated, at 20°, against a standard meter. The carriage bearing the fine, horizontal reading line, ruled on glass, could be moved up or down on the stiff steel rod (diameter 20 mm.) which formed its support. A mirror, behind the glass tubes and extending the entire length of the gage, eliminated errors due to parallax in reading. Three thermometers were suspended at intervals along the gage. That they might show the same temperature lag as the mercury in the arms of the manometer, their bulbs were immersed in mercury

Fig. 1.—Static isoteniscope.

Fig. 2.—Pressure gage.

[1] Before being erected, the gage was repeatedly exhausted to a pressure of 0.02 mm. Its reading was checked, at frequent intervals, against a standard barometer. In setting up the gage, care was taken to make the scale exactly vertical.
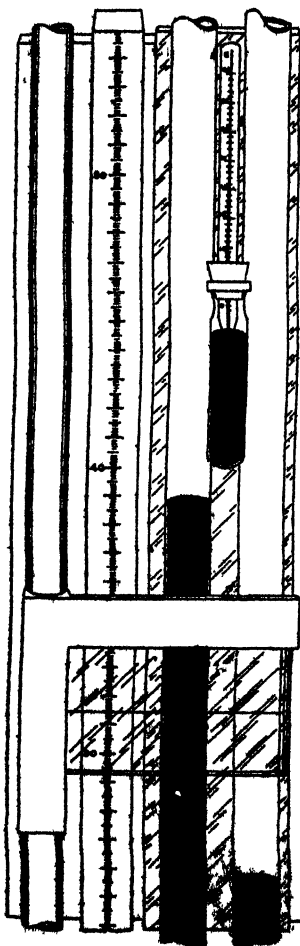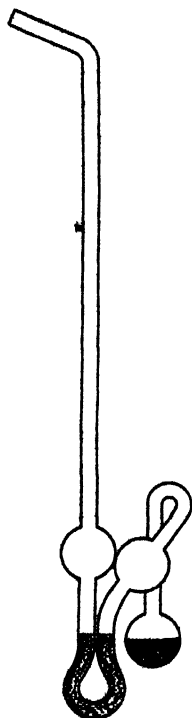
contained in small tubes (see figure). The mercury used in the gage was purified by spraying it eight times through a column of 8% nitric acid[1] and then by distilling it twice in a slow stream of air.[2] The pressures were reduced to 0° and the sea level at 45° latitude.

The temperature measurements were made with a resistance thermometer, of the Heräus type. The platinum coil is embedded in quartz. The leads are of gold and are uncompensated. This simple form of thermometer shows almost no temperature lag. In the calibration, which was repeated at frequent intervals, the procedure adopted by the Bureau of Standards[3] was used throughout. The standard resistances and bridge ratios were combined in the dial decade box of Leeds-Northrup. The coils were of manganin for which the temperature coefficient of resistance is low.[4]

The temperature scale is that based upon the ice point, steam point and sulfur boiling point, the latter being taken as 444.7° (constant volume nitrogen scale). The temperature error is less than ±0.2° at the highest readings.

The liquids used in the heating bath, and the temperatures at which each is suitable, are as follows: water, 0—70°; paraffin, 60—190°; fused sodium nitrite (10 parts), sodium nitrate (19 parts), and potassium nitrate (33 parts), 190–300°; eutectic mixture of nitrates of potassium and sodium (equimolar), 218–500°.

The bath vessel was a two-liter Jena beaker, of the tall form, jacketed by a glass battery jar from which the bottom had been removed. The 2 cm. space between the beaker and the battery jar was closely packed with asbestos wool, two small windows being left on opposite sides and about midway between top and bottom. To increase the accuracy of leveling the liquid in the isoteniscope, a fine wire was stretched horizontally across the front window and an electric light was placed just behind the other. The brass stirrer consisted of four propellors attached to a vertical shaft driven by a high speed motor. The bath was heated by a vulcan burner. With a divided gas stream and screw clamps, the supply of gas could be so controlled as to keep the temperature constant for a considerable time, to within ±0.1°, even above 400°.

Ammonium Bromide.

Previous Determinations.—F. M. G. Johnson,[5] using the spiral manometer, has determined the dissociation pressures of three ammonium halides. In regard to his temperature measurements, the following points[6] should

[1] Method of Hildebrand, This Journal, 31, 933 (1909).

[2] Method of Hulett and Minchin, Physic. Rev., 21, 388 (1905).

[3] Waidner and Burgess, Bull. Bur. Standards, 6, 150 (1909).

[4] Ostwald-Luther, [3] 412.

[5] F. M. G. Johnson, Z. physik. Chem., 65, 36–40 (1909).

[6] For a detailed discussion see Smith and Menzies, This Journal, 32, 1456 (1910).

be noted: (1) The heating bath, of air, was unstirred; (2) the dissociating substance and the glass spiral, in which the pressure was registered, were kept at different temperatures; (3) the temperatures were read by means of mercury thermometers, either of the ordinary type or nitrogen-filled. The untrustworthiness of mercury thermometers at high temperatures need not be pointed out; (4) no satisfactory provision was made for removing water vapor and gases adsorbed by, or adhering to the substances and the interior of the apparatus.

The Present Measurements.—The sample of ammonium bromide used by us was purified by recrystallization and then by sublimation. The confining liquid in the isoteniscope consisted of fused silver bromide, to which had been added ammonium bromide sufficient in amount to lower the melting point from $426°$ to $255°$. This mixture was without visible action on the vapors formed by the dissociation.

After the raising of the pressure until the boiling of the ammonium bromide ceased, there was observed a slow, uniform increase in the pressure of the vapor. Thus at $388.9°$, the pressure rose 650 mm. in ten minutes, 2 mm. in the following 10 minutes, and approximately 2 mm. in each of the succeeding ten-minute periods. The enormous difference in the rates of increase shows that there must be some secondary change. The slow increase may be due to a dissociation of hydrogen bromide (produced in the primary dissociation) and the removal of either the hydrogen or bromine by the confining liquid. Or, more probably, it may be due to the dissociation of ammonia. It is well known that the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$ occurs as the temperature rises, and that at $327°$, for example, the equilibrium, if reached, would leave over 90% by volume of the free elements[1]. In any case, the increase is very slow, and we have eliminated its effect altogether by correcting all pressure readings back to the time zero, at which the boiling out ceased. This is illustrated in the table below, which gives the readings in a preliminary experiment at $388.96°$:

Time (min.)	10	20	30	40	50		Zero
Pressure (mm.)	675 2	677 4	678 9	680 5	682 3	Mean	673 4
ΔP . .		2 2	1 5	1 6	1 8	1 8	(calc.)

The deviations in the value of ΔP from the mean (1.8 mm.) correspond to temperature differences of less than $0.03°$, which is about the limit of accuracy in the temperature control. The size of the correction factor decreased as the temperature was lowered. For an entire series of pressures and temperatures the correction averaged 1.1 mm. That Johnson did not detect this increment of pressure is probably due to the fact that it is close to the limit of sensibility of the spiral manometer, said by him to be "of the order of 1 mm."

[1] Haber and Van Oordt, Z. anorg. Chem., 44, 356 (1905)

The Results.—Two series of measurements were made. When the results were plotted out a large piece of cross-section paper, the points were found to lie closely along a smoothed curve. Three points on this curve (320°, 100.6 mm.; 370°, 404.8 mm.; and 397°, 806.9 mm.) were used to evaluate the constants in the Kirchhoff-Rankin-Dupré formula, log p = —A/T + B log T + C. This equation, with the constants introduced, becomes

$$\log p = -2056.541/T + 9.54014 \log T - 20.98468.$$

Since points calculated from the equation must lie exactly on a perfectly smooth curve, the irregularities in the individual pressures and temperatures observed can be shown by the magnitude of their deviations from the values found from the formula. Table I gives the observed pressures (Col. 1), those of the second series of measurements being distinguished by the asterisk; the observed temperatures (Col. 2); the temperatures calculated from the above formula (Col. 3); and the differences (Δ) between the observed and the calculated temperatures. The temperatures are given to the second decimal place, because in comparing the values, this figure is significant.

TABLE I —DISSOCIATION PRESSURES OF NH$_4$Br—OBSERVATIONS.

Press. Mm.	Temperature.			Press. Mm.	Temperature.		
	Obsd.	Calcd.	Δ.		Obsd.	Calcd.	Δ.
928.6*	402 87	402 68	+0 19	421 6	371 60	371 53	+0 07
789 3	396.21	396 17	+0.04	334.7	362 40	362 79	—0 39
792 3*	396 22	396 34	—0 12	329 9*	362 50	362 27	+0 23
662 2	389 01	389 10	—0 09	227 9	348 63	348 64	—0 01
661.9*	388 96	389 08	—0 12	131 3*	329 10	329 12	—0 02
533.9	380.50	380 61	—0 11	59 5*	303 25	302 78	+0 47
534 2*	380.57	380 65	—0 12				

The algebraic sum of the differences between the observed and the calculated temperatures is +0.02°, or close to zero, as it should be. The mean deviation of a single observation from the curve is 0.15°. The observations are therefore consistent. This deviation is within the limits of error of the absolute temperature measurements themselves (less than ±0.2°), so that the smoothed curve as a whole is probably correct to ±0.2°.

The dissociation pressures of ammonium bromide, for rounded temperatures, are given in Table II. The pressures in the second column (S. and C.) have been calculated from the formula; those in the third column (J.) have been read from a large curve plotted from the results of F. M. G. Johnson. This table shows, as do also the curves (Fig. 3), that the differences between our results and those of Johnson become large at the higher temperatures, at which a mercury thermometer is especially unreliable. At 394.6° this difference is 45 mm.
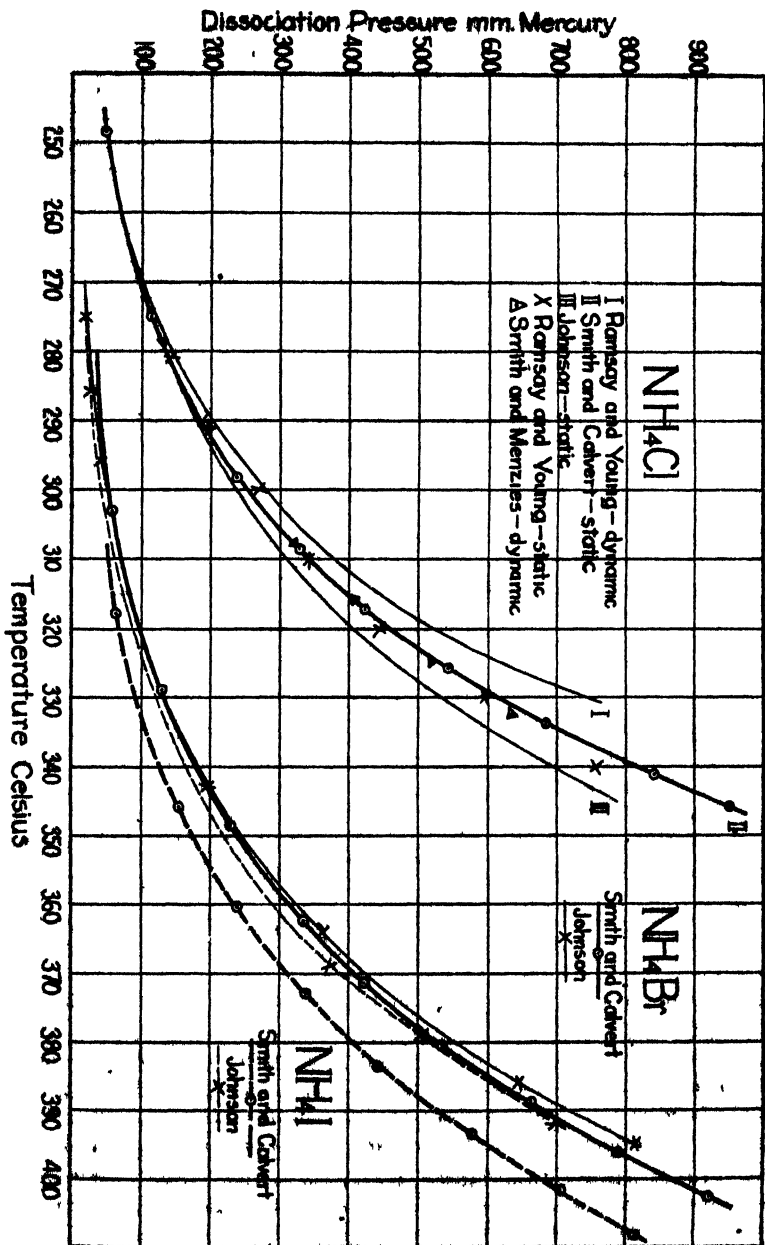
Fig. 3.

TABLE II.—DISSOCIATION PRESSURES OF NH₄Br, AT ROUNDED TEMPERATURES

	Pressure.			Pressure.	
Temp	S. & C.	J.	Temp.	S. & C	J.
300	55 0	56	380	525 5	548
320	100 6	101	390	677 5	718
340	178 8	180	394 6	760.0	805
360	310 4	316	400	868 4	
370	404 8	421	403	935 1	.

Ammonium Iodide.

The Present Measurements.—A C. P. ammonium iodide was purified by recrystallization and dried by heating *in vacuo* at 100°. It was not resublimed because, at high temperatures, it is decomposed by moist air with the formation of free iodine. Sublimation of a substance to be used in the isoteniscope is really unnecessary. The repeated boiling out, before each reading, removes the volatile matter; non-volatile matter does not affect the vapor pressure of the solid, unless contained in solid solution.

The confining liquid was fused silver iodide (m. p. 530°)[1] to which had been added an equal weight of ammonium iodide. The mixture froze at 260°.

In the heated vapor of ammonium iodide the following changes occur

$$NH_4I \rightleftarrows NH_3 + HI$$
$$2HI \rightleftarrows H_2 + I_2$$
$$2NH_3 \rightleftarrows 3H_2 + N_2$$
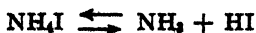
The hydrogen iodide[2] and ammonia dissociate very slowly. Since we desired to measure the pressure due to ammonium iodide and its primary dissociation products only, we have eliminated the effect of the slow, uniform increase in pressure produced by the secondary changes. The data below, taken from a preliminary observation at 346°, will show the method. The time is expressed in minutes after the boiling out ceased.

Time (min) ..	10	20	30	40	50	60	70
Pressure (mm.)	164 1	165 2	166 1	166 5	166 7	167 2	167 6
ΔP		1 1	0 9	0 4	0 2	0 5	0 4

The mean value of ΔP is 0.6, and the pressure at zero time, therefore, 163.5 mm.

As was to be expected, the correction factor became larger at the higher temperatures, at which slight traces of free iodine could be detected in the isoteniscope. Johnson observed a rise in pressure of 10 mm. per hour at 357°. Although he worked rapidly, the accumulation of free iodine

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[1] Landolt and Börnstein, *Tabellen*, [4] 229.

[2] At 350° and 380 mm. pressure, hydrogen iodide is dissociated to the extent of 4% after 24 hours' time. Bodenstein, *Z. physik. Chem.*, 13, 117 (1894).

in the spiral during an entire series of pressure and temperature readings must have been considerable.

The Results.—From the final temperature-pressure readings a large, smooth curve was constructed. A Kirchhoff-Rankin-Dupré formula, for this curve, was calculated from the following fundamental points; $340°$, 130.3 mm.; $380°$, 407.3 mm., $400°$, 675.2 mm. The equation, with the constants evaluated, is

$$\log p = -7714.591/T - 10.04345 \log T + 42.69560.$$

Table III gives, for each pressure, the temperature observed, the temperature calculated from the formula, and the difference (Δ) between the two values. In two cases only does the difference exceed $0.14°$.

TABLE III —DISSOCIATION PRESSURES OF NH_4I—OBSERVATIONS

Press Mm.	Temperature.			Press Mm	Temperature		
	Obsd.	Calcd.	Δ.		Obsd	Calcd	Δ
830 3	408 54	408 63	+0 09	335 6	372 69	372 73	+0 04
704 6	401 74	401 77	+0 03	238 0	360 33	360 34	+0 01
699 3	401 38	401 43	+0 05	153 3	345 93	345 35	—0 58
576 5	393 63	393 57	—0 06	156 1	345 79	345 93	+0 14
452 9	384 06	384 07	+0 01	64 0	317 80	318 05	+0 25
339 3	372 99	373 13	+0 14		Algebraic sum		+0 12

The equilibrium pressures for ammonium iodide at rounded temperatures, are given in Table IV. The pressures in the second column (S. & C.) have been calculated from the formula; those in the third column (J.) have been read from a large curve plotted from the data of F. M. G. Johnson.[1]

TABLE IV —DISSOCIATION PRESSURES OF NH_4I AT ROUNDED TEMPERATURES

Temp	Pressure		Temp	Pressure	
	S & C	J		S & C	J.
310	48 5	67	380	407 3	512
330	95 0	127	390	527 0	662
350	176 3	219	400	675 2	
360	235 7	291	404.9	760.0	. .
370	311 5	384	410	857 0	

As seen from the table, and also from the curve (Fig. 3), the pressures found by Johnson are much higher than those found by us for the same temperatures This difference is 18 mm. at $310°$ and 135 mm. at $390°$. As stated above, the pressures given by Johnson probably include considerable partial pressures of hydrogen and iodine produced by the dissociation of hydrogen iodide, especially at the higher temperatures.

Ammonium Chloride.

Previous Determinations.—The dissociation pressures of ammonium chloride have been determined by a number of investigators but with

[1] Since the pressure-temperature points of Johnson are rather irregular, we have smoothed the curve as indicated in the small figure in his dissertation (Breslau, 1908).

only fair agreement between the results. The spiral manometer, as used by F. M. G. Johnson,[1] has been described and discussed under ammonium bromide, above.

Ramsay and Young have measured the dissociation pressures by two widely different methods. In the dynamic method,[2] a thermometer was inserted into a hole bored in a block of solid ammonium chloride. Then the block, with the thermometer, was placed in a combustion tube heated to about 30° above the probable temperature of sublimation for ammonium chloride. The pressure in the combustion tube could be varied at will. When the thermometer reading became constant, it was considered that the surrounding solid was at the sublimation point for that particular pressure. In the static method[3] of Ramsay and Young, ammonium chloride was heated and the vapors confined over mercury. The hydrogen chloride produced in the dissociation reacted with the mercury at a rate which necessitated a rather large correction for the change of pressure with time. Another source of uncertainty lay in the slow diffusion of the mercury vapor into the vaporization chamber. The authors ascribe to thermometric errors the differences in the values found by the two methods. At the highest temperatures, this difference amounts to 100 mm.

Smith and Menzies[4] have determined the dissociation pressures of ammonium chloride by the dynamic isoteniscope, alkali nitrates being used as the confining liquid. The vapors acted chemically on the fused nitrates, and the production of a gas made impossible the adjustment of the pressure until the bubbling entirely ceased. Their experiments were intended especially to show the value of the isoteniscope even when used under unfavorable conditions.

The Present Measurements.—The measurements were repeated, partly for the purpose of using the *static* isoteniscope with this substance, partly because results covering a wider range of temperature were desired, and partly in order that the pressures and vapor densities (the latter to be determined subsequently) might be correlated by using identical samples of ammonium chloride and thermometers calibrated in exactly the same manner.

For most of the readings, the confining liquid here used was a fused mixture of silver chloride and ammonium chloride, in approximately equal parts by weight. This liquid froze at 290°. At 275°, the liquid employed was recrystallized bismuth; at 249°, it was Kahlbaum's tin. Oxidation of these metals was prevented by displacing the air in the appa-

[1] Z. physik. Chem., **61**, 458 (1908)

[2] Ramsay and Young, Phil. Trans., **177**, 96 (1886). This method had been used previously by Horstmann, Ber., **2**, 137 (1869).

[3] Ramsay and Young, Phil. Trans., **177**, 86 (1886).

[4] THIS JOURNAL, **32**, 1457 (1910).

rates at the beginning with illuminating gas. All pressures were read ten minutes after the "boiling out" had been stopped and were corrected to the time zero by subtracting the uniform increment of pressure found for succeeding ten-minute intervals. The correction factors averaged less than 1 mm.

The Results.—Table V contains: the observed pressures (Col. 1), those of series 2 being marked with an asterisk; the observed temperatures (Col. 2); the temperatures calculated (Col. 3) from the equation for the smoothed curve, log p = —1920.357/T + 9.778609 log T —21.21708; and the differences (Δ) between observed and calculated temperatures (Col. 4). The vapor-pressure formula given above is based on the following points: 280°, 135.0 mm.; 312°, 362.4 mm.; 338°, 764.8 mm.

TABLE V.—DISSOCIATION PRESSURES OF NH$_4$Cl—OBSERVATIONS.

Press. Mm.	Temperature.			Press. Mm.	Temperature.		
	Obsd.	Calcd.	Δ.		Obsd.	Calcd.	Δ.
949.6	345.91	345.86	+0.05	422.9*	317.35	317.26	+0.09
949.5*	345 96	345 84	+0.12	326.7	308.45	308.53	—0.08
840 8	341.35	341.43	—0.08	325.8*	308 37	308 43	—0 06
826 7*	340 90	340 82	+0.08	238.5	298.16	298.15	+0.01
711 5*	335 41	335.43	—0.02	238.1*	298 11	298 08	+0 03
684.4	334 08	334.04	+0.04	114.2	275.00	274.85	+0.15
544 2	325 85	325.95	—0.10	113.8*	275 5	274.75	+0.40
546.6*	325.82	326.09	—0.27	49 5	248.46	249.99	
424 1	317 27	317.35	—0.08		Algebraic sum		+0.30

It will be seen that the differences between observed and calculated temperatures are greater than 0.1° for only five of the seventeen observations. At the lowest temperature there is a large deviation (1.53°) which corresponds to a pressure difference of 2.6 mm. Much more weight is here to be given to the calculated than to the observed temperature, since the tin, used as confining liquid at this one temperature only, reacted with the vapor. The dissociation pressures, for rounded temperatures, are tabulated below[1] (Table VI).

TABLE VI.—DISSOCIATION PRESSURES OF NH$_4$Cl AT ROUNDED TEMPERATURES.

Temp.	Press.	Temp.	Press.
250	49.5	320	458.1
270	97.5	330	610.6
280	135.0	337.8	760.0
290	185.3	340	808.2
300	252.5	345	927.6
310	341.3	350	1063.0

These results and those of other observers are plotted in Fig. 3. The prediction[2] that, on account of lack of time for the attainment of full dis-

[1] For the dissociation pressures found, by other observers, for rounded temperatures, see Smith and Menzies, THIS JOURNAL, 32, 1458 (1910).

[2] Smits and Scheffer, Z. physik. Chem., 65, 70 (1908).

sociation, pressures found by the dynamic method would be very much lower than those determined by the static method has not been realized. That the pressures by the dynamic methods would be slightly lower is obvious, since the substance, which is boiling slowly, must be cooled somewhat below the temperature of the surrounding bath. The pressures (dynamic) of Smith and Menzies[1] are, on the average, lower than are those found by us (static) by 7.5 mm.

Tetramethylammonium Chloride.

Previous Observations.—Practically nothing is known of the temperatures at which the tetraalkyl-ammonium salts sublime. This may be due to the fact that, before the submerged bulblet was described,[2] the organic chemist had no convenient method for the accurate determination of the boiling point of a non-fusing solid.

With regard to tetramethylammonium chloride, Lawson and Collie[3] state that it "decomposes above 360°," yielding trimethylamine and methyl chloride. The reaction is similar to that for the dissociation of an ammonium halide.

$$N(CH_3)_4Cl \rightleftharpoons N(CH_3)_3 + CH_3Cl.$$
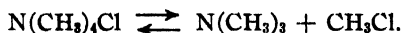
Wagner[4] says that tetramethylammonium chloride "begins to decompose at 230° and volatilizes rapidly at 280°." Our results show the equilibrium pressure at the lower of these temperatures to be nearly one atmosphere.

The Present Measurements.— The confining liquid was mercury, which had been carefully purified by spraying several times through dilute nitric acid and then distilling twice. During the period of 45 minutes, which was the average time required to obtain equilibrium, the mercury vapor was able to diffuse back to the surface of the subliming solid. Thus the total pressure observed was the sum of the partial pressures of mercury and of tetramethylammonium chloride. At each temperature, the corresponding vapor pressure of mercury has therefore been subtracted from the observed pressure. The pressure to be subtracted varied, according to the temperature, from 11.0 to 43.1 mm., and was obtained by linear, interpolation from the final table of Smith and Menzies.[5]

The tetramethylammonium chloride was purified by recrystallization from alcohol. It was dried, for a day, at 100° and then pulverized.

A difficulty arose in the very slow rate at which the system solid–vapor reached equilibrium. At 245°, for example, the pressure reached only 182 mm. during the first hour, although the equilibrium pressure for this

[1] Smith and Menzies' temperatures, based on the scale S. B. P. = 445 0° have been reduced, for the purpose of this comparison, to the scale S. B. P = 444 7°.

[2] Smith and Menzies, THIS JOURNAL, 32, 897 (1910).

[3] J. Chem. Soc., 53, 624 (1888).

[4] Z. Krystall. Min., 43, 179 (1907).

[5] THIS JOURNAL, 32, 1447 (1910); Ann. Physik, [4] 33, 988.

temperature is more than 760 mm. Two methods of producing equilibrium in a shorter time present themselves: first, the use of a suitable catalyzer and, second, the heating of the substance to a high temperature in order to obtain a large pressure of the dissociation products and then cooling until recombination begins to occur. The second procedure[1] was adopted. It is illustrated by the following, typical set of readings which was obtained in one of the preliminary experiments:

Temp.	Press	ΔP (per 10 min) Mm	Change
228 7°	660 5	+11 0	Dissociation
228 2°	662 5	+ 2 6	Dissociation
227 8°	661 0	0 2	Combination
227 85°	661 0		Equilibrium

At lower temperatures the dissociation was even slower than in the foregoing example, and the individual readings are therefore probably less accurate than are those obtained with the simple halides. It is estimated, however, that the temperatures (absolute) read from the smoothed curve (Fig. 4) are accurate to less than ±0.4°.

$N(CH_3)_4Cl$ $N(CH_3)_4I$
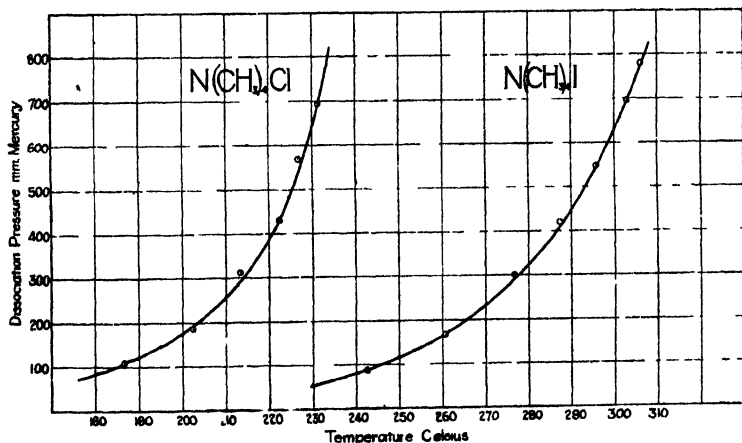
Fig 4

The Results.—Table VII shows, for each pressure, the temperature observed, the temperature calculated from the Kirchhoff-Rankin-Dupré formula, and the differences (Δ). The formula is based on the following points on the curve: 190°, 119.4 mm.; 220°, 398.0 mm., 230°, 641.8 mm. The equation, with the constants introduced, is

$$\log p = 23649.7/T + 132.316 \log T - 401.3121.$$

[1] This method has been used by us in earlier, unpublished experiments, on the dissociation of mercuric oxide It has since been described by Taylor and Hulett, *J Phys Chem.*, **17**, 571 (1913)

TABLE VII.—DISSOCIATION PRESSURES OF N(CH₃)₄Cl—OBSERVATIONS

Press. Mm.	Temperature.			Press. Mm.	Temperature.		
	Obsd.	Calcd.	Δ.		Obsd.	Calcd.	Δ.
690	231.5	231.5	0.0	312	213.3	214.4	—1.1
567	227.1	227.4	—0.3	187	202.4	202.3	+0.1
430	222.5	221.6	+0.9	108	186.6	186.8	—0.2

The mean deviation of the observed points from the smooth curve represented by the equation is 0.4°. Readings from the curve (or calculations from the equation), relatively to one another, should therefore be accurate to within ±0.2°.

The equilibrium pressures, calculated from the formula, for rounded temperatures, are as follows:

Temp............	190°	200°	210°	220°	225°	230°	233.3°
Pressure (mm.)...	120	171	256	399	504	643	760

Tetramethylammonium Iodide.

Lawson and Collie[1] state that "decomposition" of tetramethylammonium iodide occurs "at a temperature not much short of a low red heat." According to Wagner,[2] "decomposition begins" at 230°.

The Present Measurements.—The dissociation pressures were determined by means of the static isoteniscope, with the eutectic mixture of the nitrates of sodium and potassium for confining liquid. The tetramethylammonium iodide was purified by recrystallization from water. Its vapors had no action on the molten nitrates.

The pressure in the isoteniscope, at each temperature, was found to rise at a very rapidly decreasing rate for a few minutes. Then the increase in pressure became slower and almost uniform. Thus, in a preliminary experiment, at 276.0°, the change in pressure with the time, after the boiling out process was stopped, was as follows:

Time (min.)..... .	0	5	10	15	20	25	50
Pressure (mm). ..	224.9	308 7	326.6	338.5	344.1	349.8	375.7
Δ P.......	...	83.8	17.9	11.9	5.6	5.7	5 × 5.2

The consideration of the time-pressure curve shows clearly that the rapid rise in the pressure for the first 15 minutes and the slower increase during the next 35 minutes cannot be due to the same cause. It seems certain also that the rapidity of the first change must be due to the dissociation into trimethylamine and methyl iodide.

$$N(CH_3)_4I \rightleftharpoons N(CH_3)_3 + CH_3I$$

Then the methyl iodide, in turn, undergoes decomposition, a change observed by Lawson and Collie,[1] and confirmed by the darkening of the tetramethylammonium iodide and the walls of the isoteniscope

[1] Loc. cit.
[2] Z. Kryst. Min., 43, 180 (1907).

during measurement. That the confining liquid played no part in this decomposition was shown by substituting bismuth and various alloys for the nitrates. In each case the same results were obtained. Also, the darkening of the material and isoteniscope occurred in parts of the apparatus never reached by the confining liquid. Since we desired only the pressure of the undissociated molecules and of the primary dissociation products of the salt, we have corrected all pressures, read at the end of the period of rapid increase, back to the time when the "boiling out" was stopped. The method used is described in the section on ammonium bromide.

The Results.—The temperatures and corrected pressures were plotted, on a large scale, and a smoothed curve (see Fig. 4) was drawn to fit the observations. From three points on this curve (264°, 188 mm.; 290°, 455 mm.; 302°, 678 mm.) the following equation was derived:

$$\log p = 1493.085/T + 24.96449 \log T - 68.65910$$

The results are tabulated in the form already described.

TABLE VIII.— DISSOCIATION PRESSURES OF $N(CH_3)_4I$—OBSERVATIONS.

Press. Mm.	Temperature.		Δ.
	Obsd.	Calc.	
781	306.2	306.1	+0.1
698	303.0	302.8	+0.2
547	295.8	295.5	+0.3
421	287.4	287.7	—0.3
298	276.6	277.5	—0.9
166	260.6	260.6	0.0
88	242.6	242.3	+0.3

The following data show the pressures, calculated from the equation, for rounded temperatures:

Temp.	240°	260°	280°	290°	300°	305.5°	307°
Pressure (mm.)	81	164	325	455	635	760	790

Phosphonium Iodide.

Previous Observations.—Phosphonium iodide, when warmed gently, volatilizes rapidly and dissociates according to the equation:

$$PH_4I \text{ (solid)} \rightleftarrows PH_4I \text{ (gas)} \rightleftarrows PH_3 + HI.$$
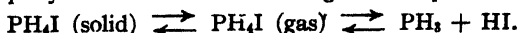
F. M. G. Johnson[1] has measured the dissociation pressure at various temperatures, a fact which came to our attention only after our measurements were completed. A *stirred* water bath was used for heating the bulb containing the phosphonium iodide and the attached spiral manometer. Since the temperatures were all below 62°, the errors due to the mercury thermometer and to the shifting of the zero-point of the glass spiral were at a minimum. The chief sources of uncertainty which characterized

[1] THIS JOURNAL, **34,** 877 (1912).

Johnson's earlier vapor-pressure measurements (with the exception of the adsorbed gases), were thus eliminated. Our results are published, partly, to show the concordance in the values obtained by the isoteniscope and the spiral manometer when the necessary precautions are used in both cases. Confirmation of Johnson's work seems desirable, also, since his results lower the boiling point of phosphonium iodide from 80°, the commonly accepted value,[1] to 62°.

The Present Measurements.—The static isoteniscope was used, fractionated benzyl benzoate serving as the confining liquid. The fraction chosen had a vapor pressure of 718 mm. at 310°, 329 mm. at 280°, and 53 mm. at 220°. The curve connecting these points shows that, at 66°, benzyl benzoate would have a vapor pressure lower than that of mercury, which is negligible at this temperature.

As the result of some recent investigations, Holt and Meyers[2] have concluded that, in carefully dried phosphonium iodide vapor, there occurs a secondary reaction in which the hydrogen iodide and phosphine give some free hydrogen and phosphorus iodide. Such a change was indicated in our experiments by a slow, uniform increase in the pressure with the time. Correction has been made for this effect. Holt and Meyers state that phosphorus iodide is not formed if a trace of moisture is present. For this reason, perhaps, Johnson obtained no evidence of its formation. His method did not provide with certainty for the removal of the last trace of moisture (and foreign gases) from the spiral manometer and from the material in the vaporization chamber.

The Results.- The results obtained by us are tabulated below (Table IX).

TABLE IX.—DISSOCIATION PRESSURES OF PH_4I—OBSERVATIONS.

Series I.		Series II.	
Press. (Mm.).	Temp.	Press. (Mm.).	Temp.
914.0	65 92	922.1	66.22
795 0	63.47	798.3	63.52
662.8	60.13	667.7	60.08
532.6	56.06	533.2	56.19
401.2	51.29	408.7	51.46
301.0	46.69	301.9	46.58
195 3	39.82	196 0	39.78
109.0	30.63	118 1	31.01
39.3	16.08	40.9	16.98

The agreement between the values found by Johnson (J.) and those by us (S. & C.) is shown for rounded pressures in Table X (see also Fig. 5).

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[1] Abegg, "Handb. anorg. Chemie," Vol. III, Pt. 3, p. 398; Moissan, *Chim. Min.*, I, 758.

[2] *Z. anorg. Chem.*, **82**, 281 (1913).

TABLE X.—DISSOCIATION PRESSURES OF PH$_4$I—ROUNDED VALUES.

Dissoc. Press.	Temperature.		
	J.	S. & C.	Δ.
50	19.26	19.21	+0 05
100	29.33	28 92	+0 41
200	39.89	40 09	—0.20
300	46.40	46.55	—0.15
400	51 08	51.16	—0.08
500	54.94	55.02	—0.08
600	58.16	58.20	—0.04
700	60.73	61.10	—0.37
760	62.00	62.61	—0.61
800	...	63.56	...
900	...	65.68	...

PH$_4$I

○ Smith and Calvert
× Johnson
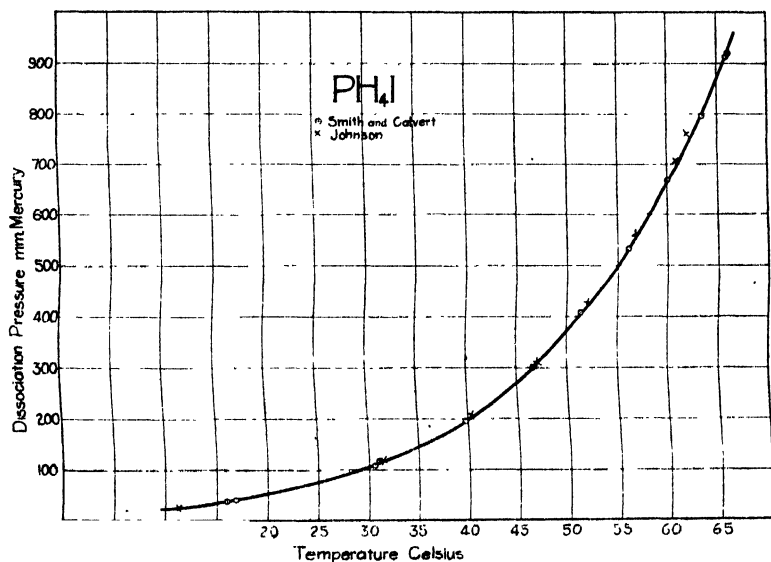
Fig. 5.

The dissociation pressures read for rounded temperatures, from our curve are:

Temp.	15°	30°	40°	50°	60°	62.6°	66°
Pressure (mm.)	36.0	107.8	199.0	368.1	660 0	**760.0**	917 5

Phosphorus Pentachloride.

Previous Observations.—Although there has been much work and discussion on the dissociation of the superheated vapor of phosphorus pentachloride, neither the pressure nor the density of the vapor in equilibrium with the solid phase has ever been determined. The sublimation

point for phosphorus pentachloride, based on qualitative work of Cas-selmann,[1] is usually given as 140–148°. Recently, Prideaux,[2] by intro-ducing a thermometer into vapor of phosphorus pentachloride, found the vapor to condense at a temperature of 160°. This he accepts as the lower limit for the sublimation point. The upper limit is the melting point, found by him to be 162°. Our work gives somewhat higher values for both the boiling and the melting point. This was to have been expected, since, in our experiments, the repeated fractionation expels the last traces of all volatile impurities.

The Present Measurements.—Since the chlorinating power of phosphorus pentachloride is extremely high, it was very difficult to find a suitable confining liquid. A fused mixture of saturated chlorides might be expected to have no action on the vapors. We were unable, however, to devise such a mixture, of melting point sufficiently low, that was not hygroscopic or that had no considerable vapor pressure of its own. Other liquids tried were the eutectic of silver and thallium nitrates (m. p. 67°), the eutectic of silver and potassium nitrates (m. p. 131°), purified mercury, sulfur, and paraffin. Paraffin, the least active, was chosen for the final experiments. The sample of paraffin used was freed from its more volatile constituents by heat-ing at 200°, under a pressure of 20 mm. for an hour. It was then placed in the *dynamic* isoteniscope in which slow interaction between the vapor and confining liquid can be neglected.[3]

The phosphorus pentachloride is contained in the small bulb to the right (Fig. 6). To obtain a read-ing, the pressure in the isoteniscope is lowered until the pentachloride sublimes rapidly, giving a rapid stream of bubbles through the paraffin. Then the pressure is raised until the point is reached at which the vigorous bubbling ceases. The pressure required to stop the sublimation is the vapor pressure for that particular temperature. The readings are not so accurate as are those taken with the static isoteni-scope since bubbles of gas continue to be produced *slowly*, as a result of the interaction of the paraffin and phosphorus pentachloride. However, the bub-bling due to boiling is so much more vigorous than

Fig. 6.—Dynamic iso-teniscope.

that due to secondary chemical action that it is not difficult to determine, with fair accuracy (± 5 mm.),

[1] *Lieb. Ann.*, **83**, 257 (1852).
[2] *J. Chem. Soc.*, **91**, 1714 (1907).
[3] Smith and Menzies, This Journal, **32**, 1457 (1910).

when the former ceases. A small correction must be applied for the depth to which the tip is submerged below the surface of the paraffin and for capillarity in the tip.[1]

The sample of phosphorus pentachloride used was the product of a standard manufacturer. The impurities suspected were the trichloride (b. p. 76°) and oxychloride (b. p. 107–110°). These impurities were removed from the phosphorus pentachloride, after it had been placed in the bulb of the isoteniscope, by lowering the pressure to 30 mm. and keeping the temperature of the surrounding bath at 120° until over half of the sample had been volatilized. It may safely be assumed that, in this way, all the easily volatile impurities were driven out past the paraffin seal. This conclusion was confirmed by the fact that subsequent boiling out did not alter the pressure found at a given temperature. Nonvolatile impurities would have no effect on the vapor pressure, so long as any pure phosphorus pentachloride remained as solid phase.

The Results.—The results are tabulated in the usual form.

TABLE XI.— DISSOCIATION PRESSURES OF PCl_5—OBSERVATIONS

Press. (Mm.).	Obsd.	Temperature. From curve.	Δ.
31	98.08	98.13	—0.05
60	108.31	108.22	+0.09
158	126.10	125.96	+0.14
219	132.71	133.00	—0.29
347	143 68	144.02	—0.34
492	152.42	152.46	—0.04
608	157 63	157.69	—0.06
748	162 58	162.30	+0 28
915	166.89	(liquid)	..

The phosphorus pentachloride melted at a point just below the last temperature observed. As was to have been expected, the pressure (marked +, Fig. 7) of the liquid (915 mm. at 166.89°) fell considerably below the corresponding point on the smoothed curve for the vapor pressure of the solid (= 1.0°, equivalent to about 40 mm.).

The dissociation pressures for rounded temperatures are:

Temp..........	90°	120°	140°	150°	,160°.	162.8°	167°
Pressure (Mm.).	18	117	294	445	670	760	919(liq.)

The heats of vaporization for the various substances will be calculated after the degrees of dissociation have been determined.

Summary.

1. The dissociation pressures of seven substances have been determined for the following ranges of temperature and pressure: NH_4Br

[1] For the simple method of finding the sum of these corrections, see Smith and Menzies, THIS JOURNAL, **32**, 1449 (1910).

(300°–403°; 35–935 mm.), NH$_4$I (310°–410°; 48–857 mm.), NH$_4$Cl (250°–350°; 50–1063 mm.), N(CH$_3$)$_4$Cl (190°–233.3°; 120–760 mm.), N(CH$_3$)$_4$I (240°–307°; 81–799 mm.), PH$_4$I (19.2–65.7°; 50–900 mm.), PCl$_5$(90–167°; 18–919 mm.).
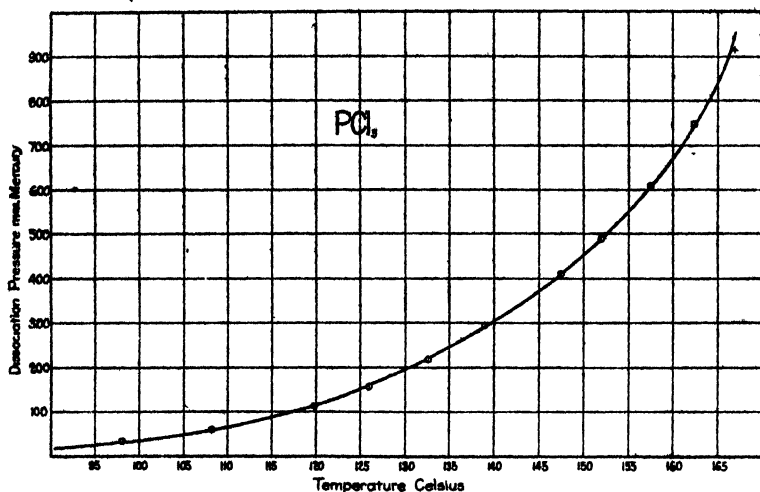
Fig. 7.

2. The measurements on PCl$_5$ were made with the dynamic isoteniscope; all the others with the static isoteniscope, by means of which the pressure may be determined to ±0.1 mm. A platinum resistance thermometer sensitive to ±0.1° was used.

3. The temperatures at which the various compounds were found to have a dissociation pressure of 760 mm. are: NH$_4$Br (394.6°), NH$_4$I (404.9°), NH$_4$Cl (337.8°), N(CH$_3$)$_4$I (305.5°) PH$_4$I (62.6°), and PCl$_5$ (162.8°).

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
    COLUMBIA UNIVERSITY, NEW YORK CITY

POSITIVE IONS FROM NON-METALLIC ELEMENTS. I. A STUDY OF THE PRECIPITATION OF METALS FROM SOLUTIONS OF THEIR SALTS BY YELLOW PHOSPHORUS.

BY R. M BIRD AND S. H. DIGGS
Received April 23, 1914

Introduction.

It has long been known that yellow phosphorus will precipitate certain metals (Pt, Au, Ag, Hg, Cu) from a solution of the salts of these metals. Berzelius made use of the fact that silver is completely precipitated from

its salts by phosphorus to determine the combining weight of phosphorus.[1]

In 1836, Vogel stated that when phosphorus acts on a solution of copper sulfate, there is formed sulfuric acid, phosphoric acid, and phosphide of copper only.[2]

Straub (1903) made a study of this reaction, and found that, in all cases studied by him, phosphoric acid, sulfuric acid, phosphide of copper, and metallic copper were formed. He determined the ratio of the sulfuric acid to the phosphorus in the solution as phosphoric acid at the end of the reaction and found it in several experiments to be as follows: 8.2, 7.6, 7.9, 6.4, 7.4, 7.5 and 8.0; to 1.

From this he concluded that one atom of phosphorus displaces two atoms of copper from solution. (The figures are, however, far nearer to 2.5 Cu to 1 P.) He tried to find a ratio between the copper sulfate and the total phosphorus (i. e., the phosphorus in solution and that combined as phosphide of copper), but his results were so very irregular that he concluded the reaction must proceed by steps, and that no equation could be written to express it.[3]

Christomas,[4] Tauchert,[5] Corne,[6] Granger,[7] and others worked on this or similar reactions of phosphorus. Though all of these workers proposed equations that seemed probable, none were in very close accord with the experimental data. Nor did any of them, so far as we can find, propose any explanation of the mechanism of the reaction.

The Problem.—In spite of the fact that phosphorus is looked upon as a typical non-metallic element, the precipitation of certain metals by it in apparently the same way in which one metal is precipitated by another metal higher in the "potential series" seemed worthy of careful work to determine if the phosphorus reaction is ionic or not. The analogy to such a reaction as zinc displacing copper under similar conditions is very striking. Such reactions are probably always ionic. Apparent exceptions, such as the reduction of ammoniacal solutions of silver by aldehydes, are almost certainly electrolytic also.[8]

Choice of the Metallic Salt.—While silver is precipitated quantitatively, its use is objectionable because of the fact that the only practical salt to use is the nitrate, and nitric acid, even when dilute, will appreciably act on yellow phosphorus. The chlorides of copper and mercury were tried and rejected, because in both cases the "ous" salts are formed and afterwards

[1] Berzelius, *Gilbe.t's Ann.*, 53, 433; *Pogg. Ann.*, 8, 17.

[2] Vogel, *J. prakt. Chem.*, 8, 109.

[3] Straub, *Z. anorg. Chem.*, 35, 460 (1903).

[4] Christomas, *Z. anorg. Chem.*, 41, 307 (1904).

[5] Tauchert, *Ibid.*, 79, 350 (1912).

[6] Corne, *J. Pharm. Chim.*, 6, 323.

[7] Granger, *Compt. rend.*, 122, 1484 (1897).

[8] Compare Stieglitz, "Analytical Chemistry" (theoretical part), Vol. 1, p. 3.

decomposed. This introduced an unnecessary complication. Sulfuric acid, even when of $\frac{g}{4}N$ strength and boiling hot, did not appreciably act on phosphorus; so that all things being considered copper sulfate seemed the best salt with which to work.[1]

Plan of the Work.—The plan of the work was:

(a) To make a complete analysis of solutions after sticks of yellow phosphorus had been left in them for a sufficient time.

(b) To determine the equation which represents the reaction, if possible.

(c) To make a study of the probable mechanism of the reaction by physical-chemical methods.

Experimental.

Qualitative Results.—1. About 200 cc. of 0.5 N copper sulfate was placed in a glass-stoppered Erlenmeyer flask and several small sticks of clean yellow phosphorus were dropped into it. After about a week, the *solution* was analyzed and found to contain:

Copper....	None
Phosphoric acid..	In large amount
Phosphorous acid.	Appreciable
Hypophosphorous acid....	Doubtful
Sulfuric acid.........	In large amount

The *precipitate* was found to be:

(a) Chiefly a bright, clean tube of metallic copper surrounding the stick of phosphorus.

(b) A thin inside coating of black phosphide of copper, next to the phosphorus.

Many experiments were carried out to determine the effect on the reaction of varying the concentration of the copper sulfate solution, and also the effect of the sulfuric acid formed during the reaction. Greater and less concentrations of acid were studied in order to magnify its effects. The following partial summary of these experiments indicates all the kinds of results which were obtained:

PARTIAL SUMMARY OF QUALITATIVE EXPERIMENTS.

2. Copper-sulfate, 0.5 N, equal vol. conc. H_2SO_4	(At once and after 24 hrs.)	Film copper-phosphide, trace H_2PO_4
3. Copper-sulfate, diluted H_2SO_4		Same as 2
4. Copper-sulfate, further dilutions of acid	(After 60 hrs.)	Copper-phosphide, phosphoric acid, trace Cu-salt in sol.
5. Copper-sulfate, sulfuric acid stronger than N		Metallic copper, splotches of phosphide, H_3PO_4, etc.

[1] In one experiment phosphorus was permitted to remain in equivalent strength of copper sulfate and sulfuric acid for about five months without a ___ of phosphorus dissolving in the sulfuric acid, and without any further solution of the phosphorus in the copper sulfate than corresponds to the reactions here given.

6. Copper-sulfate, 0.5 N, equal vol. with N to 0.25 N	(After 24 hrs.)	Metallic copper only, H₃PO₄ etc. (same as 1)
7. ½ Copper-sulfate, acid considerably under 0.25 N	(After 24 hrs.)	Copper, spots of phosphide, H₃PO₄, etc.
8. Copper-sulfate, acid, very dilute	(After 24 hrs.)	Copper-phosphide, little copper, H₃PO₄ etc
9 Copper sulfate only, 0.5 N and other moderate dilute sols.		Metallic copper only (at first), H₃PO₄, etc. (same as 1)
10 Copper-sulfate, very dilute sols		Copper, more or less phosphide, H₃PO₄, etc
11 Precip. copper, bright and clean, in distilled water or original sol.		Layer of phosphide next to phosphorus increasing with time until no copper remains. No further sol. of P in H₂O
12. Copper-sulfate, 0.5 N, equal vol 2.5 N NH₃ sol.	(After 24 hrs)	Dead black coating, no copper seen No Cu-salt left in sol.

Quantitative Results. The Determination of the Acids of Phosphorus.—The phosphoric acid was determined as magnesium pyrophosphate. In all cases 10 cc. samples were used   Separate samples were oxidized very thoroughly with hydrogen peroxide and then the phosphoric acid determined as before.   The results agreed closely and averaged:

Mg₂P₂O₇ before oxidising	Mg₂P₂O₇ after oxidising
0 1106 g.	0 1198 g
0 4968 milli-mols	0 5382 milli-mols.

Hence the number of gram atoms of *lower* acids of phosphorus in 10 cc. is $(0.5382 - 0.4968) = 0.0414 \times 2 \times 10^{-3}$. That is, 0.0828 milli-mols of lower acids in each 10 cc. of the solution.

In other samples, after the sulfuric acid had been precipitated as barium sulfate, the clear filtrates were treated with an excess of mercuric chloride to determine the quantity of lower acids of phosphorus.   The precipitated calomel weighed 0.0315 g. If we assume the lower acid of phosphorus to be *phosphorous* acid, this corresponds to 0.0669 milli-mols; if, however, we assume the reducing acid to be *hypophosphorous* acid it corresponds to only half as many mols.[1]

A fresh sample, treated with an excess of common salt and mercuric chloride, gave 0.0370 g. of calomel. This corresponds to 0.0783 milli-mols of reducing phosphorous acid.

[1] If we assume that *only* phosphoric acid is formed, we should have enough total acid (sulfuric and phosphoric) in 10 cc. of the solution to neutralize 60 cc. of 0.1 N alkali when using methyl-orange as indicator, and 70 cc.

when using phenolphthalein as indicator. The difference should be 10 cc. and corresponds to one-third of the phosphoric acid present. (This is calculated on the basis of the analysis previously given.)

Three separate samples were titrated with accurately standardized NaOH solution. The results were the same in all to within 0.1 cc. and averaged as follows: with phenolphthalein, 69.5 cc. and with methyl-orange, 58.5 cc. That is, the difference between the titration figures using phenolphthalein as indicator and those using methyl-orange as indicator is 11 cc. whereas we should theoretically expect 10 cc. While this method is far from an exact one, it indicates that about 10% of the total acids of phosphorus present were other than phosphoric. This is in rough agreement with the results found by the calomel method.

The Determination of Sulfuric Acid.—A determination of the sulfuric acid (as barium sulfate) showed that the SO_4 content had not changed; *i. e.*, the sulfuric acid had not been reduced.

The original solution contained 2 5 milli-atoms of copper in 10 cc.; hence, we have very nearly 5 atoms of copper displaced by 2 atoms of phosphorus.[1]

The Formation of Copper Phosphide.—Some of the sticks of phosphorus that were completely covered by a bright coating of metallic copper were removed from the solution and placed in a jar of distilled water. In a few weeks the copper had entirely disappeared and there remained nothing but a mass of phosphide of copper and phosphorus. This convinced us that *the formation of the phosphide of copper is a secondary reaction taking place between the metallic copper and phosphorus*, and not between the sulfate of copper and phosphorus, as was thought by Straub, Tauchert and others.

Probable Reactions.—The quantitative results show that the atomic ratios involved are, in round numbers, 5 of copper to 2 of phosphorus. The simplest equation that will represent this fact is,

$$5\,CuSO_4 + 2P + 8H_2O = 5Cu + 5H_2SO_4 + 2H_3PO_4.[2]$$
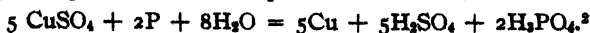
The reaction given above is undoubtedly the essential reaction involved, but this does not tell anything of the nature of the reaction or the role played by phosphorus in it.

The Origin of the Lower Phosphorus Acids.—It is known that yellow phosphorus will reduce phosphoric acid, partly, to phosphorous and hypophosphorous acids. This we believe to be the way in which the *-ous* acids

[1] $2.5/2(0 4968) = 5/2$.

[2] The ratio of the phosphorus to the sulfuric acid involved in the above reaction is 1 to 7.9. This is about the same as Straub found, but he was so sure that a phosphide was first formed that he interpreted his figures to give *two* atoms of copper to *one* of phosphorus, instead of the far more accurate value of *five* atoms of copper to *two* of phosphorus. The reaction as we have deduced it is given by Tauchert as being one of several reactions that take place more or less simultaneously. He, too, believed that a phosphide of copper was directly formed from the sulfate.

in the analyzed solutions originated. For, if this be correct we should expect to find *less* phosphoric acid than is indicated by the given reaction and *more* total phosphorus in solution than is thus indicated. This is in accord with the figures given on page 1385 and the fact that the quantity of lower acids increases with time. On the whole, the origin of the phosphorous acid is not of very great importance for our investigation.

Physical Chemical Data.

1. It was observed that the metallic copper was formed only on the *surface of the phosphorus, or on the surface of a conductor connected with the stick of phosphorus*. That is, the phosphorus and any *conductor* connected with it becomes *plated* with copper, just as would be the case if iron or zinc were used in place of the phosphorus. In no case did metallic copper form on the surface of the glass beaker or any other *non-conductor* connected with the phosphorus. A piece of platinum wire wrapped around a stick of phosphorus, and extending upwards in the solution, becomes well plated with copper for a distance of several centimeters above the phosphorus.

2. Two side-neck test tubes were joined by means of a piece of rubber tubing; in one was put about 5 cc. of 0.5 *N* copper sulfate and in the other an equal quantity of 0.5 *N* silver nitrate. A piece of phosphorus was put into the *silver nitrate* and joined by means of a platinum wire to the copper sulfate solution. (See Fig. 1.) Both tubes were then filled with magne-
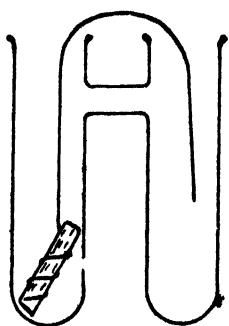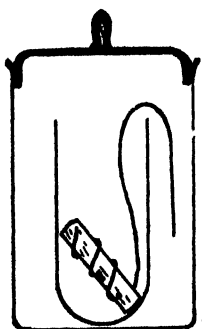
Fig. 1.   *Fig. 2.*

sium sulfate solution. The wire in the copper sulfate soon became coated with copper, and in about two weeks all copper and silver had been thrown out of solution. A control experiment, in which the platinum wire was used without phosphorus showed no reaction.

Similar experiments were performed using a porous alundum cylinder in a glass-stoppered weighing flask. (Fig. 2.) The results were identical

with those obtained in the above described experiment, except that the action was much more rapid. A control experiment without the phosphorus gave no precipitate of metal.

These facts and the analytical data strongly indicate an electrolytic displacement. The phenomena cannot be explained on the theory of a concentration cell, because of the negative results from the control experiments, and also because of the fact that when a platinum wire is wrapped closely around the phosphorus and does not extend out into the solution, both wire and phosphorus become heavily plated with metal.

Explanation of the Phosphorus-Copper Cell.—The qualitative experiments discussed above convinced us that phosphorus and copper really do form a true cell, just as any two metals do. This seems improbable at the first glance because of the position of the two elements in the published "potential series," and of the supposed non-existence of positively charged phosphorus ions. However, we adopted the following as a working hypothesis:

(a) The phosphorus goes into solution to an infinitesimal extent as P^{+++++} ions, thus leaving the stick of phosphorus charged negatively. Owing to the exceedingly small solution pressure of phosphorus, the number of such ions would be small relatively to the ions formed in the case of ordinary metals, the latter even being very small.

(b) These positively charged phosphorus ions react with the relatively abundant hydroxyl ions (of the water) to form phosphoric acid almost completely. This caused the concentration of the positively charged phosphorus ions to be exceedingly small, *but not zero*.

(c) If the negative charge on the stick of phosphorus is neutralized (say, by the Cu^{++} ion), then more phosphorus must go into solution in the effort to re-establish equilibrium. This, in turn, will react with the hydroxyl ions present to form more phosphoric acid and water. This would continue until one of the reacting substances became exhausted, or until the concentration of the hydroxyl ions becomes small in comparison with their usual concentration in water. This would be the case in very strongly acid solution, and this may be the explanation of the fact that phosphorus did not precipitate copper appreciably in very strongly acid solution.

The electromotive force of the phosphorus-copper cell is given by the formula,

$$E = 0.0577 \ (1/5 \ \log P_1/p_1 - 1/2 \ \log P_2/p_2)$$

where P_1 is the solution pressure of phosphorus, and p_1 the osmotic pressure of the P^{+++++} ion; P_2 the solution pressure of copper, and p_2 the osmotic pressure of the Cu^{++} ion.[1]

The value of P_1 is unknown, and there is reason to believe that the solution pressure of cupric copper is smaller (relatively) than is commonly

[1] Nernst, "Theoretical Chemistry," pp. 753–759.

supposed. Be this as it may, the solution pressure of phosphorus is certainly even smaller, but p_1 is so very small in comparison with p_2 that we may expect E to be positive; i. e., we may expect phosphorus to be the *negative* electrode with respect to copper, just as iron would be. The reason however, is different; for in the case of iron it is due to a larger solution pressure and in the case of phosphorus to a smaller *osmotic* pressure.

The above hypothesis looks upon phosphorus *as playing the same role as do metals while passing into solution* from the solid form.

A phosphorus sulfate (analogous to the zinc sulfate in a Daniell cell) is not formed because phosphorus functions so weakly as a base that such a salt, if formed, would be immediately hydrolyzed, just as the chlorides of phosphorus are known to be.

If the hypothesis outlined above be tentatively accepted, the reaction between phosphorus and copper sulfate becomes easy to explain; it is simply an interchange of ionic charges, which might be expressed thus:

$$5Cu^{++} + 2P = 5\ Cu + 2P^{+++++}$$
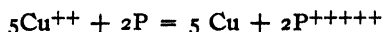
in the same sense that we write

$$3Cu^{++} + 2Al = 3Cu + 2Al^{+++},$$

or

$$Cu^{++} + Zn = Cu + Zn^{++}$$
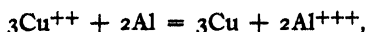
The equation which expresses the reaction between phosphorus and copper sulfate would be

$$5CuSO_4 + 2P + 10H_2O = 5Cu + 2H_3PO_4 + 5H_2SO_4 + 2H_2O.$$
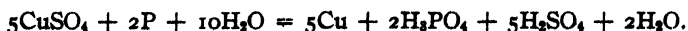
Or, so far as concerns the formation of phosphoric acid it would be

$$2P^{+++++} + 10(OH)^- = 2P(OH)_5 = 2H_3PO_4 + 2H_2O.^{[1]}$$
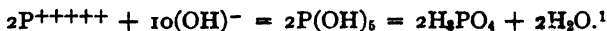
Measurement of the E. M. F. of the Phosphorus-Copper Cell.—In order to further test the above explanation of the reaction, cells were made consisting of a copper electrode immersed in 0.5 N copper sulfate and a phosphorus electrode immersed in various solutions, including those from which all copper had been precipitated by phosphorus.

The apparatus used is illustrated by Fig. 3. The copper electrode was of the usual type, and the phosphorus electrode consisted of a glass tube into one end of which a platinum wire was sealed, and the tube filled with melted phosphorus. There was in all cases at least 3 cm. and usually 5 cm. of phosphorus below the end of the wire. This work had to be done carefully, as the least leak gave, virtually, a platinum instead of a phos-

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[1] An analogous reaction where a positive ion passes into solution and immediately reacts with negative ions already present to yield a negative ion, is seen in the case of silver dissolving in potassium cyanide-solution; our measurements showed that the undissolved silver is charged negatively while the solution is taking place.

phorus electrode.[1]   Out of more than a dozen of such electrodes only three showed appreciable leaks.   These were discarded.

The measurements were made by means of a high resistance potentiometer, a sensitive galvanometer of the D'Arsonval type, and a standard Weston cell.

Experiments were made at temperatures ranging from 0° to the melting point of phosphorus; and with samples of phosphorus that were new and colorless as well as with some that had been in the laboratory for many years.
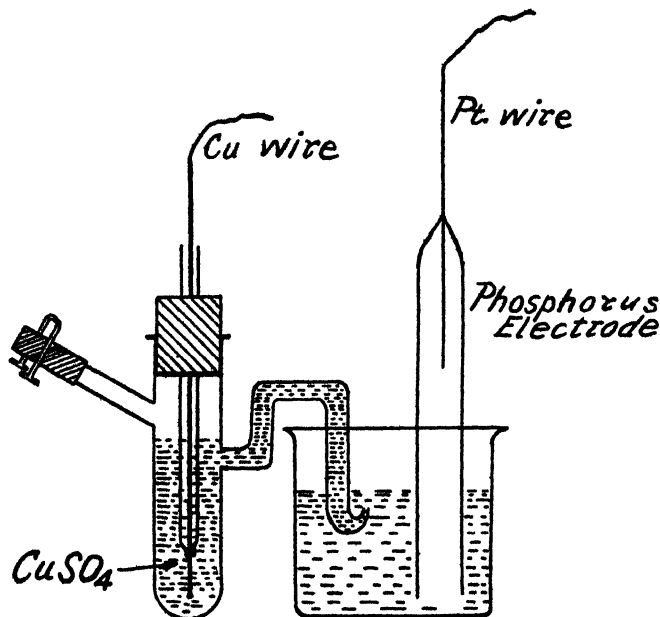

Fig. 3.

Readings were made during a period of more than four months, using new and old electrodes, some having been exposed to diffused daylight till the color had changed to a red-brown.   *In all cases the phosphorus was negative to copper*, and the E. M. F. was about 0.35 volt.   It is believed that the true value is somewhat higher, and that the irregularities are due, for the most part, to a very small leakage.   The very small conductivity of phosphorus makes important a leakage that is ordinarily negligible.

Little or no difference was to be found between immersing the phos-

[1] It is easy to know if there is a bad leak, as the platinum electrode is *positive* to the copper, *i. e.*, the polarity of the cell is reversed.

phorus in sulfuric acid of concentrations varying from 0.000001 N to 5 N. There was also little difference between distilled water and solutions of magnesium sulfate, sodium sulfate, or that from which the copper had been precipitated by phosphorus.

Values of E. M. F. of the Phosphorus-Copper Cell, Using Various Samples of Phosphorus and Various Solutions in which to Immerse it. Readings Extending Over a Period of Four Months.

Phosphorus electrode immersed in the solution from which the copper had been precipitated by phosphorus:

      0.296,   0.296,   0.306,   0.308,   0.319.

Phosphorus immersed in distilled water. (No reading at first instant, but in a few minutes giving the following values. Two different electrodes were used at different times.)

      0.275; 0.335.

      In 0.000001 N sulfuric acid; 0.380.

      In 0.001 N sulfuric acid; 0.334, 0.330.

All other recorded values are given below. Various electrodes and solutions were used, as already stated.

0.301	0.355	0.430	0.383
0.330	0 370	0.430	0.361
0.324	0.344	0.382	0.409
0.302	0.405	0.387	0.414
0.257	0.340	0.374	0.370
0.300	0.372	0 340	0.365
0.330	0.354	0.360	0 374
0.280	0.398	0.330	0 400
0.320	0.350	0.343	0 400
0.310	0.340	0.320	0.450
0.347	0.399		

It will be noted that the latter values are on the whole markedly higher than those first taken. This is believed to be due to the greater care taken to prevent electrical leaks, particularly by carefully drying and greasing the outside of the tube containing the phosphorus electrode.

These values include all measurements made, except in those few cases in which actual leaks were found, in which case the reading was reversed, just as for a copper-platinum cell. With a poorly made cell the readings were in the above direction, but low. For the sake of completeness, all of the latter readings are given below; they were made with different solutions at different times.

    0.170,   0.174,   0.106,   0.193,   0.203,   0.036,   0.020,   0.030,   0.141.

Some Precautions to be Noted in Measuring the E. M. F. of the Phosphorus-Copper Cell.

1. Owing to the very high resistance of phosphorus it is necessary to use a high resistance potentiometer and a sensitive galvanometer.

"2. Care must be taken to secure a balance as quickly as possible, because experience shows that the cell is easily polarized, i. e., if we draw current from it for an appreciable time the voltage drops, or if the current passes the other way it rises. Using storage cells it was found possible to "charge" the phosphorus electrode till an E. M. F. of nearly a volt was obtained, and by reversing the current the E. M. F. fell to about 0.1 volt. It slowly recovered its normal condition in both cases, however.

3. It should be remembered that very small electrical leaks (of a kind not usually important) are fatal to good results.

Conclusion.

This work, and some other not yet completed, seems to sustain our conclusion in a very definite manner. We, therefore feel, justified in saying that in displacing certain metals from their salts, phosphorus first passes into solution as a positively charged ion, in the same way as do the metallic elements. We further believe that the chief distinction between the so-called non-metallic elements and the metallic elements depends upon their tendency to hydrolyze and the subsequent ionization of this product, rather upon their ability to form positive ions.[1]

Note.

In order to see whether or not the above is a general reaction of the non-metallic elements, and to throw light upon the electrochemical character of their oxygen acids, experiments are now being conducted with the following: vanadium, arsenic, antimony, bismuth, sulfur, selenium, chromium, molybdenum, tellurium, tungsten, iodine, carbon, silicon and boron. Cells like Fig. 2 are being used and there have been obtained precipitates of metallic silver on a pure gold wire in contact with *amorphous carbon, amorphous boron, crystalline silicon, antimony and arsenic*, immersed in 0.01 N silver nitrate solution—one solution only being used inside and outside the porous thimble. Check solutions with silver nitrate and nitric acid but without the non-metallic element have shown no precipitates. Carbon yields carbonic acid; the others have not yet been analyzed.

The reactions of *solutions of phosphorus* in various solvents in contact with solutions of salts are also being studied in light of the above results.

An effort is being made to obtain a comparable potential series of all elements and to determine if those elements (both metallic and non-metallic), which exhibit different valences occupy more than one position in the series.

University of Virginia,
    University, Va.

[1] See the note which follows. Also, for a different discussion of the part played by positive ions in reduction and oxidation reactions, as well as a discussion of certain ions that are little known, see "Qualitative Chemical Analysis," Vol. I, by Julius Stieglitz.

FLUIDITY AS A FUNCTION OF VOLUME, TEMPERATURE AND PRESSURE. THE EQUATION OF STATE, AND THE TWO KINDS OF VISCOUS RESISTANCE SO-CALLED "SLIPPING" OF GASES.

[PRELIMINARY.]

BY EUGENE C. BINGHAM.[1]

Received April 24, 1914.

Fluidity and Volume.

Attention[2] has been repeatedly called to the intimate relationship which exists between the fluidity of a liquid and its volume. Batschinski[3] has recently given this relationship quantitative expression. According to him

$$\eta = c/v - w$$

where η is the viscosity of the liquid, v the specific volume, and c and w are characteristic constants for the given liquid. In terms of the fluidity $\varphi = 1/\eta$, we have

$$v = w + c\varphi \qquad (1)$$

or, the volume is a linear function of the fluidity, w being the *limiting volume* toward which the volume approaches as the fluidity approaches zero. If, following Batschinski, we call $v - w$ the *free volume*, the law may be stated in the very simple form, *the fluidity of a liquid is directly proportional to its free volume*. Batschinski has found remarkable agreement between the observed and calculated viscosities for a large number of liquids, it apparently making no difference whether the change of volume is produced by altering the temperature or the pressure. For a range of temperature extending from 0° to the boiling point, or even beyond the ordinary boiling point, the differences seldom exceed 1%, except with associated substances such as the alcohols, which are exceptional, here as elsewhere.

The above law is really an extension of the law already given,[4] expressing the relation between the fluidity of a suspension and its volume concentration. The volume concentration of the medium, c_2, in which the fluidity of the suspension becomes zero, corresponds to the volume where the fluidity becomes zero in pure liquids. If m_2 represents any volume concentration of the medium, then $m_2 - c_2$ corresponds to the free volume,

[1] For earlier papers of the author on this general subject (cf. *Phys. Rev.*, **35**, 407 (1912)); [2] **1**, 96 (1913); *Z. physik. Chem.*, **83**, 641 (1913); *Trans. Chem. Soc.*, **103**, 959 (1913); *J. Phys. Chem.*, **18**, 157 (1914); *J. Ind. Eng. Chem.*, **6**, 233 (1914)).

[2] *Am. Chem. J.*, **35**, 215 (1906); **43**, 290 (1910); **45**, 268 *et seq.* (1911); *Z. physik. Chem.*, **83**, 655 (1913).

[3] *Ann. de la Soc. d'encouragement de sciences experimentales et des leurs applications au nom de Christophe Ledenzoff, Suppl.*, **3** (1913); *Z. physik. Chem.*, **84**, 643 (1913).

[4] *Phys. Rev.*, **35**, 421, *et seq.* (1912).

and the fluidity of the suspension is directly proportional to the free volume.' From equation (9)[1] of an earlier paper by the author we get,

$$\varphi = (w_2 - c_1)\varphi_2/c_1 \qquad (2)$$

which is evidently a more explicit form of equation (1) above. In suspensions the medium has a finite fluidity, hence the fluidity of the suspension φ cannot exceed the fluidity of the medium φ_2. Pure liquids may be regarded as suspensions in space, of infinite fluidity, so that there is apparently no limit to the fluidity which may be obtained by indefinitely increasing the volume. A further point of interest in this connection, is the fact that the concentration of its zero fluidity in a suspension, is independent of the temperature or of the nature of the medium.

The Equation of State.

If, in van der Waals' equation,

$$(p + a/v_2)(v - b) = RT,$$

we substitute for the volume its value in terms of $w + c\varphi$, we obtain a formula in which the fluidity, temperature and pressure are variables. Since, however, the pressure is constant under the usual conditions of viscosity measurement, this relation becomes

$$T = A\varphi + C + B/\varphi + D - E/(\varphi + D)_2 \qquad (3)$$

in which A, B, C, D and E are constants. Over any ordinary range of temperature, this formula may be simplified. In fact, the author has already shown[2] that the formula

$$T = A\varphi + C - B/(\varphi + D) \qquad (4)$$

will reproduce the observed fluidities of all the liquids tested with very great accuracy. For all but the most highly associated liquids, or over a very wide range of temperature, the formula may be still further simplified to

$$T = A\varphi + C - B/\varphi \qquad (5)$$

and satisfactory results obtained. Thus for seventy substances, the average deviation between the observed and calculated values of the absolute temperature is only 0.09%. For a highly associated substance like water, the average deviation is 0.17%, but with Formula (4) it becomes only 0.01%.

In a similar manner one obtains a formula for the pressure in terms of the fluidity

$$p = \alpha T/(\varphi + \beta) - \gamma/(\varphi + \delta)^2. \qquad (6)$$

When the fluidity or the temperature is very great, the second term of the right-hand member becomes negligible and the formula represents an equilateral hyperbola. Large fluidities and high temperatures presum-

[1] *Phys. Rev.*, **35**, 423 (1912).

[2] *Z. physik. Chem.*, **66**, 251 (1909).

ally belong to the gaseous state and, as van der Waals' equation applies best to gases where the volume and temperature are great, we might look for a similar fluidity relation. That any such expectation is doomed to disappointment is proved by Clerk Maxwell's observation that the fluidity of a gas over a short range of pressures and temperatures is independent of the pressure, which has been repeatedly confirmed. Thus Equation (1) applies to liquids but certainly not to rarefied gases. The cause of this interesting peculiarity may well engage our attention next.
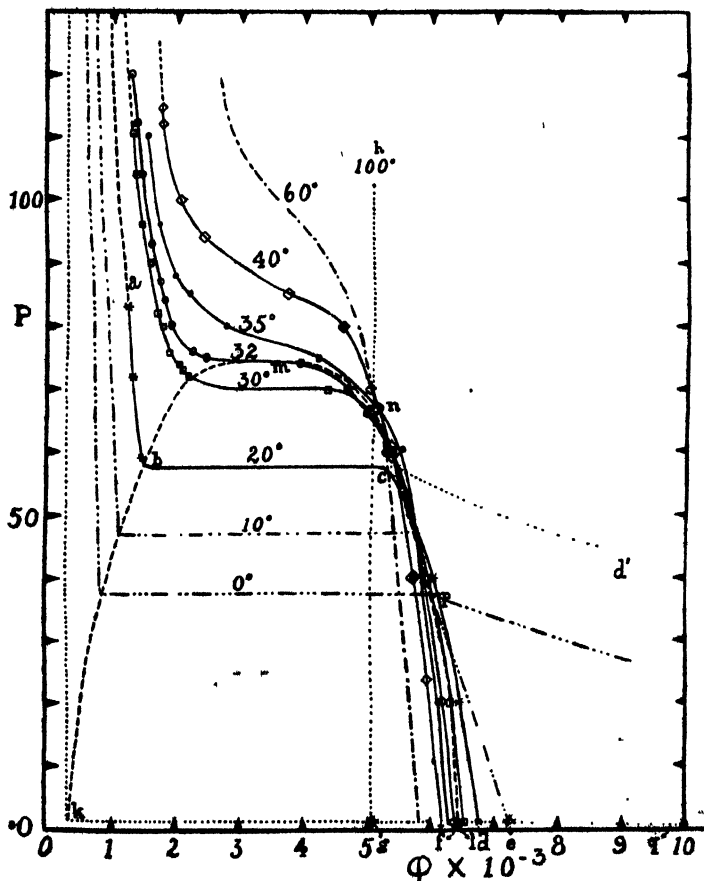
Fig. 1.—Pressure-fluidity curves of carbon dioxide.

In Fig. 1 are drawn the pressure-fluidity curves for carbon dioxide for the temperatures measured by Phillips.[1] The curves are drawn as

[1] *Proc. Roy. Soc.* (*London*), 87A, 48 (1912).

continuous lines between the observed points. · The broken lines have been added for diagrammatic purposes. The left half of the figure, which corresponds to low fluidity and temperature, presents a striking similarity to the familiar pressure-volume diagram. At the highest pressures, the fluidity is not greatly affected by a change in the pressure, e. g., at 32° and a pressure of 120 atmospheres, a lowering of the pressure by four atmospheres causes an increase in the fluidity of less than 4%. At a lower pressure the fluidity is extremely susceptible to changes in pressure, a lowering of the pressure by four atmospheres at 76 atmospheres, causing an increase in the fluidity of a full 100%. Both the gaseous and liquid phases are present in the region inside of the Curve *kbmcl*. The right side of the figure is quite different from the familiar pressure-volume diagram. Instead of the fluidity being highly susceptible to changes in pressure, it is but slightly affected, e. g., at 32° and 50 atmospheres pressure, a lowering of the pressure by four atmospheres causes only a 10% increase in the fluidity. Let us now consider carbon dioxide at 20° which is well below the critical value. At high pressures the fluidity increases linearly from *a* to *b*; there is then a sudden increase in the fluidity from 1500 to 5300 C. G. S. units, as the substance passes from the liquid to the gaseous condition. We should expect the fluidity to continue to increase as the pressure is further lowered, giving the Curve *cd'*, but the curve actually obtained is *cd*. It is generally true that the fluidity of liquids increases with the temperature, while, on the other hand, the fluidity of gases decreases with the temperature, hence the pressure-fluidity curves for different temperatures must cross each other. It is interesting to note that the figure shows, that not only is this true, but, when the temperatures are sufficiently high, the curves all tend to pass through a particular point *n*; and for lower temperatures, the curves tend to intersect each other on the Curve *ncl*.

The fluidity of carbon dioxide at atmospheric pressure for 0°, 40° and 100°, as obtained from the Tabellen of Landolt, Börnstein and Meyerhoffer, are plotted at the points *e*, *f*, and *g*, respectively. If *gnh* is taken to represent the hypothetical pressure-fluidity curve of carbon dioxide at 100°, it is evident that, for this temperature, Maxwell's law holds perfectly so that the fluidity is independent of the pressure. But is it equally evident that it would hold strictly for no other temperature. At 0° the fluidity curve of gaseous carbon dioxide is approximately *pe*, while for the temperature of the ordinary boiling point of carbon dioxide the pressure-fluidity curve would apparently be *lq*, and the law breaks down entirely. What would happen if the temperature were raised far above 100° would be very interesting to learn, but the data are not available at present.

The Nature of the Two Causes of Viscous Resistance.

That the pressure-fluidity curves do not follow an equation of the van der Waals type as the fluidity increases, may be due to the appearance

as a new cause of resistance. We must therefore now inquire more particularly into the nature of viscous resistance. It has long been realized that a cause of viscous resistance in gases arises from the diffusion of the particles of layers with high translational velocity into layers whose translational velocity is lower, and *vice versa*. According to this explanation the loss of translational velocity must increase with the temperature, which accords with the fact that the fluidity of a gas decreases as the temperature is raised.

But in liquids the fluidity *increases* as the temperature is raised and it appears that there is a second cause of viscous resistance which has been repeatedly attributed to the attraction between the molecules. Batschinski[1] gives this conception expression in the following terms: "In gases, the properties which depend upon the reciprocal attraction of the molecules manifest themselves only slightly, whereas with liquids, on the contrary, these properties are of prime importance. If we may think of two parallel layers of the liquid as of two rows of men, the men moving in the place of molecules, we must require these men to take hold of their nearest neighbors and to hold them for a time."

This explanation seems to the present author to be inadequate for the following reasons: As a particle A comes within the range of attraction of a particle B in an adjacent layer supposed to be moving more slowly, the particle A will be accelerated and only after passing B will the retardation take place. I see no reason why these two actions should not exactly neutralize each other, in which case none of the translational energy will be changed into heat. But, perhaps it would be urged that the retarding influence is more like chemical combination, since the particles lay hold on each other and, in the words of Batschinski, "während einiger Zeit festhalten." If the particles of the liquid grasp and hold each other, a kind of association must result which should be detected by some physical method, and non-associated substances ought not to show any viscosity at all. As a matter of fact, not only do all liquids have viscosity, but mercury, which is usually regarded as non-associated, has a lower fluidity than many highly associated substances such as water and alcohol. This objection may be avoided by assuming that this grasping and holding of the particles is proportional to the rate of shear of the liquid, so that it is zero when the liquid is at rest; but, since the molecules are always in rapid vibrational motion, it is difficult to see how the small translational motion would affect the attraction in a way to produce the result which we observe.

In order to get a clearer idea of the nature of the two causes of viscous resistance to flow, let A and B in Fig. 2 represent two parallel planes at a constant distance apart, the space between being filled with the viscous

[1] *Loc. cit.*

substance. For the simplest case, suppose that the substance is a gas at so low a pressure that the distance from A to B is small in comparison with the mean molecular free path. Let the surface A be supposed to be moving to the right with a constant velocity in respect to the surface B which may, for convenience only, be conceived to be at rest. If the surfaces A and B were perfectly smooth and unyielding and the particles of fluid perfectly elastic spheres, we would not have a model of viscous flow; for as the particles collided with these surfaces, the angle of rebound would in each case be equal to the angle of impingement and since there is conservation of momentum, no translational motion could be transmitted to or from the walls, *i. e.*, the "slipping" would apparently in this case be perfect. In order to obtain a model of viscous flow, we are therefore obliged to make some assumption, and the simplest and most probable one is that the surfaces A and B are not perfectly smooth. In view of the known discontinuity of matter, the least degree of roughness that we could well assume, is that the surface is made up of equal spheres, all of whose centers lie in the same plane and as closely packed together as possible. That there is a greater degree of roughness in all ordinary surfaces is probable, but it suffices for our present purposes to show that this simple assumption in regard to the nature of the surfaces gives a workable model of viscous flow. In a model of viscous flow it is necesssry for the molecules striking the surface A to be given a component of velocity in the direction of the viscous flow. We shall refer to this as *translational* velocity in contradistinction from the disordered *vibrational* velocity of the molecules. The resultant translational velocity of the molecules is evidently proportional to the rate of efflux, while the *resultant* vibrational velocity is zero. It is further necessary that as the molecules strike the surface B, the translational velocity received at A should be transformed into vibrational velocity or heat, so that any resultant translational velocity would disappear in a short time were it not continually supplied at the surface A.

That the model described above meets these requirements depends upon the truth of the following theorem: *When a series of elastic particles strike a rough surface, the resultant component of velocity along the surface will be diminished.* That this is true must now be made evident. Let M, N, and P, in Fig. 3 represent the section through the centers of three of the greatly magnified spheres supposed to make up the surfaces in Fig. 2. Suppose that a small particle were to strike such a surface at any acute angle θ. It is evident that if such a particle is to strike the

sphere N in the plane of the paper, its possible paths all lie between A and G. By drawing the directions of the particle before and after collision, assuming that the angle of rebound at any point of the surface is equal to the angle of impingement, we find that for possible paths between B and D the average resultant velocity of rebound is exactly opposite in direction, although diminished in amount. For paths between A and B a particle would collide with M on rebounding from N but the component
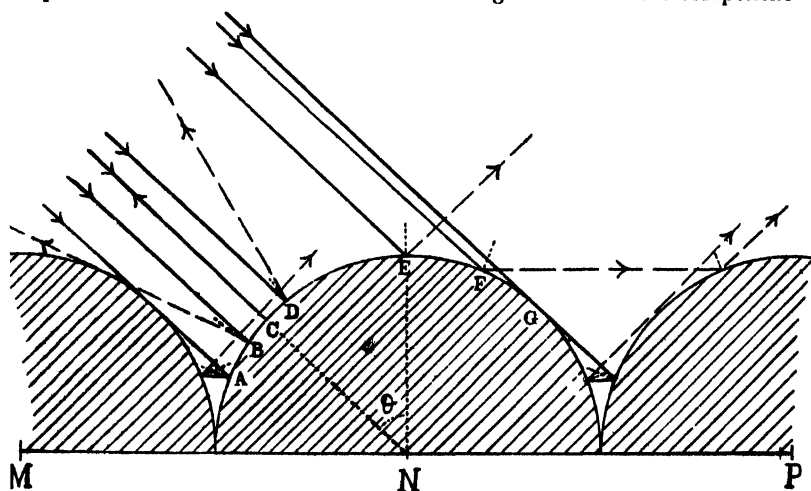

Fig 3.—A diagram illustrating how translational motion becomes changed into vibrational motion by striking a rough surface.

of the velocity in the direction NP is diminished. Also for paths between D and E, as well as between F and G, the component of the velocity in the direction NP will be diminished. Only between E and F is the component in the direction of flow greater after collision than before. But the distance EF becomes zero when $\theta = 90°$ and it has its maximum value when $\theta = 0°$, i. e., when the translational motion is zero. Since all of the paths between A and G are equally likely, it follows that for this section at least, the average translational velocity of the small particles is diminished by collision irrespective of the size of the angle or of the velocity of the particle, and it can be easily shown that the same is true even if the particle is of considerable size. The same must be true a fortiori for sections other than the one passing through the centers of the spheres, for then there must, after collision, be a component velocity at right angles to the plane of the paper and therefore to the direction of flow. The section would be similar to the one given except that the circles would not touch, the spaces between them corresponding to the pores in which the translational velocity is quite certainly changed to disordered motion.

$$\mathrm{MuNu}/6 = \mathrm{Uu}/6\rho$$

The viscosity, which is the force required when $u = 1$ and $s = 1$, is therefore

$$\eta = \rho U/6s \qquad\qquad (7)$$

which may be put into the form

$$\eta = \frac{Kp\sqrt{T}}{Sv\sqrt{M}}. \qquad (8)$$

Where p is the pressure, v the volume, T the absolute temperature, and K a constant.

The most interesting and surprising thing about the above formula is its requirement that the viscosity of a rarefied gas must depend upon the dimensions of the apparatus used, the viscous resistance increasing as the space between the two surfaces is reduced.

Collisional Viscosity.

For the opposite extreme, we may conceive of a very viscous liquid, two layers of which, C and D, are shown in Fig. 4. The appearance is the

Fig 4.

same as if a small portion taken from Fig. 2 had been greatly magnified, so that the molecules appear as disks instead of points, except that the molecular concentration is greatly increased. The effect of this increased concentration is to indefinitely decrease the molecular mean free path, so that the diffusional viscous resistance is negligible, but the actual volumes of the molecules are comparable with the spaces which they occupy and collisions are immensely more frequent.

Since the layer C is nearer the surface A (not shown) than is D, it must move more rapidly than the layer D, according to the fundamental law of viscous flow discovered by Newton. The molecules of this layer must therefore overtake the molecules of D and in colliding with them tend to impart translational motion. Thus momentum passes through successive layers from A to B, and if B is free to move, it will take up the same velocity as A, all of the molecules taking part in the translational drift toward the right. But the surface B is assumed to be at rest, hence the layer C must have a velocity toward the right which is permanently higher than that of D by a fixed amount and the molecules of C must continue to overtake the molecules of D and in so doing to impart momentum to them. But in collisions between the molecules of one layer with the molecules of another layer, we have already shown in connection with Fig. 3 that translational motion is continually being transformed into disordered motion. Hence we have here a true model of viscous flow, in which translational
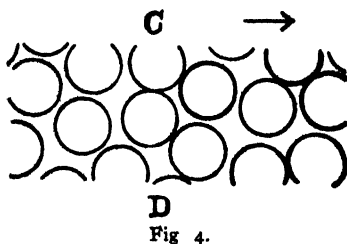
motion is continually being transformed into heat. In the extreme case, the effect of diffusion may be neglected, the viscous resistance being due solely to the collisions produced by the molecules of one layer overtaking those of another layer of smaller translational velocity. We shall refer to this as "collisional viscosity."

From the model described above we believe that it is possible to deduce the effects of changes in concentration, pressure, temperature, and size of the molecules upon this type of viscous resistance. Without attempting an elaborate proof at this time, it is probably clear that the number of collisions of the particles of one layer with those of another layer, due to their difference in translational velocity, will be directly proportional to the number of particles in each layer, i. e., to the concentration. It will also be directly proportional to the rate of shear between the layers. Temperature and pressure can effect this resistance as they affect the concentration, but not otherwise. An increase in the temperature increases the vibratory motion of the molecules but it evidently does not affect the rate at which the molecules of one layer overtake the molecules of an adjacent layer which is moving more slowly. Increasing the mass of the particles would increase the momentum of the particles and hence the viscous resistance, but we must remember that with the increase in mass there is generally an alteration in the volume. Now it is evident that the collisional viscous resistance depends both upon the actual volume of the particles and upon the volumes which these particles occupy. If the particles are to be thought of as points, there could be no collisions and therefore no collisional resistance to flow. On the other hand, if the volume of the particles themselves could be made exactly equal to the space which they occupy, collisions would be most rapid and the collisional resistance would be a maximum.

The fact that in unassociated liquids the fluidity is directly proportional to the free volume, as stated above, seems to indicate that collisional viscosity is almost entirely responsible for the viscosity phenomena of ordinary liquids. It is also clear why associated liquids are exceptional. The breaking down of association, as for example by heating, would certainly furnish cause for a change in the collisional resistance, since dissociation is usually accompanied by a change in volume, which may be either in the actual volume of the particles or in the space which they occupy or both.

The Mixed Regime.

It has been indicated that in rarefied gases viscous resistance is certainly diffusional and in very viscous liquids it is probably collisional. In gases at ordinary temperatures and pressures the viscous resistance to flow is evidently the sum of the diffusional and collisional resistances. The total viscous resistance η is in every case given by the equation

$$\eta = \eta_c + \eta_d. \tag{9}$$

In rarefied gases, the collisional resistance η_c is equal to zero and in very viscous liquids, the diffusional resistance may be negligible. In all other cases, the complete formula should be applied. The diffusional viscous resistance in this calculation does not follow the simple formula given for the model described above, in connection with Fig. 2, for the reason that the molecular mean free path affects the resistance in this case, since it affects the number of layers a molecule can pierce before it gives up its translational momentum. The diffusional viscous resistance is then proportional to the free path, which in turn is inversely proportional to the density. We found that in a rarefied gas the diffusional viscous resistance is directly proportional to the density, hence it comes about that in this case the diffusional resistance is independent of the pressure. This is the law of Maxwell, which may be formulated as follows·

$$\eta_d = 1/3\rho LU(1 + \alpha t)^n$$

where ρ is the density, L is the molecular mean free path, t is the temperature Centigrade, and U is the mean velocity. But we have seen above that

$$\eta_c = c/v - w$$

hence

$$\eta = c/v - w + 1/3\ \rho LU(1 + at)^n. \tag{10}$$

Since diffusional viscosity becomes important only when the volume is large, we may put $v - w$ for $1/\rho$. We will introduce the absolute temperature T, and for a first approximation assume that the exponent of T is unity, *i. e.*, $n = 1$. This is the value deduced from the theory by Maxwell, but experimentally determined viscosities give a value which is less than unity. But this discrepancy may conceivably be due to the collisional viscous resistance having been left out of account. We thus obtain an equation containing only three constants, which may be written in the form

$$\varphi = \frac{v - w}{A + BT(v - w)}. \tag{11}$$

This equation is very simple and convenient to apply. The following table serves to show to what extent it may be relied upon to reproduce the values obtained for carbon dioxide in both the liquid and gaseous states.

The deviations between the observed and calculated values are greatest in the critical zone where the experimental difficulties are the greatest. However, it cannot be affirmed that the agreement is within the experimental error, for apparently the deviation is systematic. But undoubtedly the agreement could have been improved by introducing another constant, as by giving the exponent of T in Formula (11) some other value than unity. It has seemed better to keep the formula in its simple form for the present.

TABLE I —THE FLUIDITY OF CARBON DIOXIDE AS CALCULATED BY MEANS OF THE FORMULA $\varphi = (v-w)/[A+BT(v-w)]$ WHERE $w = 0\ 841$, $A\ 0\ 0002578$, AND $B = 4998$, COMPARED WITH THE VALUES OBSERVED BY PHILLIPS[1] AT VARIOUS TEMPERATURES AND PRESSURES

Temp Abs	Press in atm	v	φ obs	φ calc	% Difference
293	83	1 198	1215	1152	−5
	72	1 232	1297	1241	−4
	59	1 302	1435	1418	−1
	56	5 263	5376	4890	−9
	50	6 897	5650	5299	−6
	40	10 00	6024	5734	− 5
	20	27 78	6410	6421	0
	1	546 4	6757	6907	+2
303	110 5	1 258	1299	1300	0
	104	1 280	1364	1355	−1
	96	1 316	1443	1441	0
	90	1 346	1555	1512	−3
	82	1 397	1689	1519	-11
	80	1 416	1770	1668	−6
	76	1 471	1890	1784	−6
	74	1 506	2020	1855	−8
	73	1 531	2092	1906	−9
	72	1 575	2183	1992	−9
	70	3 484	4367	4021	−8
	60	5 650	5348	4867	−9
	40	10 87	5952	5654	−5
	20	28 25	6289	6086	−3
	1	565 0	6536	6594	+1
305	120	266	1269	1318	+4
	112	287	1350	1369	+1
	104	316	1439	1439	0
	93	372	1595	1568	−2
	87	429	1706	1693	−1
	84	466	1786	1771	−1
	80	527	1894	1894	0
	76	675	2232	2168	−3
	75	802	2463	2379	-3
	74	2 778	3937	3506	−8
	70	3 922	4673	4240	−9
	60	5 882	5348	4918	−8
	40	11 111	5714	5641	−1
	20	28.41	6173	6201	0
	1	568 1	6452	6553	+2
308	114 5	1 324	1443	1455	+1
	109	1 349	1515	1512	0
	96	1 437	1706	1706	0
	88	1 531	1957	1896	−3
	85	1 597	2193	2021	−8
	80	2 024	2770	2690	−3
	75	3.460	4219	3966	−6

[1] *Loc. cit.*

TABLE I (Continued).

Temp. Abs.	Press. in atm.	v.	φ obs.	φ calc.	% Difference.
	70	4.405	4673	4425	—5
	60	6.135	5618	4943	—12
	40	11.765	5747	5642	—2
	20	28.74	6135	6135	0
	1	574.7	6410	6487	+1
313	112	1.431	1751	1686	—4
	108	1.466	1852	1759	—5
	100	1.572	2070	1965	—5
	94	1.718	2415	2221	—8
	85	2.597	3717	3302	—13
	80	3.436	4587	3920	—14
	70	4.902	5000	4553	—9
	60	6.536	5348	4964	—7
	40	12 05	5682	5585	—2
	23.8	24.51	5917	5987	+1
	1	578.0	6369	6385	0

Summary and Conclusions.

1. Attention is called to the fact that the fluidity is proportional to the "free volume," as it is called by Batschinski, not only in pure liquids and mixtures but also in suspensions of solids in liquids.

2. Since the fluidity of a liquid is proportional to the free volume, an equation resembling that of van der Waals may be used to reproduce the fluidity data as a function of the temperature and pressure.

3. Such a modified van der Waals' equation breaks down utterly when applied to gases, where *a priori* it might be expected to apply best. This discrepancy is due to the advent of an additional cause of viscous resistance in gases which does not apply in very viscous liquids. Thus the fluidity of a gas is invariably smaller than would be expected from the modified van der Waals' equation.

4. Viscous resistance in gases originates largely in the diffusion of the material which carries with it translational motion, which, in turn, by collisions becomes transformed into disordered motion. This kind of resistance to motion is called "diffusional viscosity."

5. But in viscous liquids the resistance to flow caused by diffusion is quite negligible. The resistance is shown to be due to the collisions of molecules of one layer with those of an adjacent layer moving at a slightly lower velocity. This transfer of momentum without a transfer of matter is called "collisional viscosity."

6. The viscosity of a gas or liquid is, therefore, the sum of the diffusional and collisional viscosities. We thus obtain an approximate formula $\varphi = (v - w)/[\quad RT(v - w)]$ which can be used to reproduce the observed fluidities of carbon dioxide with considerable fidelity.

7. Results are given for the belief that slipping does not occur even

in rarefied gases. The apparent viscosity of a gas as it becomes rarefied, decreases rapidly, which is entirely in accord with the theory.

8.   In gases at ordinary temperatures and pressures, the fluidity decreases as the temperature is raised, but the fluidity is nearly independent of the pressure. Both facts indicate that diffusional viscosity is of preponderating importance in gases. There is indication (cf. Fig. 1) that at very low temperatures the fluidity of gases is by no means independent of the pressure, being inversely proportional to the pressure. It is also possible that at very high temperatures the fluidity will increase with the pressure. It appears that this last has not yet been observed, but should so paradoxical a fact be discovered it would seem to offer a striking confirmation of the views here outlined.

9.   The fluidity of practically all liquids increases with the temperature and decreases with the pressure. Most liquids *expand* as they are heated or as the pressure is removed, hence we may attribute the increased fluidity to the decreased number of collisions. Sulfur and water are exceptional in their behavior, but this may be explained on the basis of association.

10.   In nearly all liquids an increase in the molecular weight causes an increase in the temperature required to produce a given fluidity, and this increase in temperature is proportional to the increase in molecular weight, in a given homologous series. There are exceptions to this generalization, such as formic and acetic acids, but the exceptions are more apparent than real, since, if we assume it to be strictly true and then calculate the association of these and other associated substances, we obtain values which are in satisfactory accord with the values given by other methods.

11.   These deductions from the kinetic theory can be extended to solids and an explanation obtained for various phenomena. The more nearly perfectly elastic a substance is, the more nearly will it come back to its original position after being strained. Movement in a perfectly elastic solid is therefore explained by the molecules of one layer, as C in Fig 4, moving up to those of another layer D, but not passing them in a single instance. Hence all of the energy is spent in producing a strictly limited amount of translational motion—the elastic limit. The energy exists as strain and as soon as the stress is removed, all of the work done is recovered, so that the process is reversible.   '

12.   When ordinary imperfectly elastic solids are subjected to stress, work is done which only partly appears as strain, a part being transformed into heat. Finally, when the stress is removed the body does not come back at once to its former position. It comes back part way and then creeps slowly toward its old position. This is the much-discussed "elastic after-effect." These phenomena may be explained as follows: When the body is subjected to stress a few of the molecules move over each other but the stress is not great enough to overcome the strains throughout the

mass and cause general flow or rupture. Wherever the molecules flow over each other heat is developed as in any viscous flow. When the stress is removed the strain tends to become immediately removed, but wherever the molecules moved over one another, the removal of the strain is hindered, the last of the strain disappearing through viscous flow under a constantly diminishing stress and therefore continuing through a long interval of time. This after-effect has been found[1] in undercooled liquids as well as solids.

13. Finally the after-effect is increased as the temperature is raised in ordinary solids and this may be explained by the expansion of the substance making it easier for the particles to move over each other in viscous flow, so that the fluidity of solids increases with the temperature as is true of most liquids. Guye and his co-workers[2] have assumed that because the vibrations in lead wires die down faster than in steel, the greater loss of energy in the former signifies that lead is more viscous than steel. Exactly the opposite conclusion seems preferable. Steel then is to be regarded as much more viscous than lead and for that very reason strains in steel are produced without nearly so much viscous flow as in lead or pitch.

RICHMOND COLLEGE, RICHMOND, VA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

IS THE DUHEM-MARGULES EQUATION DEPENDENT ON THE IDEAL GAS LAWS?

BY M. A. ROSANOFF
Received May 11, 1914

In view of the importance of the Duhem-Margules equation, in the theory of physical mixtures, no apology is necessary for raising the question as to whether it is a purely thermodynamic relationship, and therefore reliable under all circumstances, or requires modification in form as soon as vapors begin to deviate from the simple gas laws. That the latter is the case, would seem to be indicated by the fact that the gas laws are employed, at one stage or another, in every deduction of the equation that has been brought forward.[3] But closer study leads to the opposite conclusion: that the Duhem-Margules equation is absolutely general, that it must hold as true for all actual vapors, up to the critical points, as it would if the vapors behaved like ideal gases.

It is, of course, indifferent which form of thermodynamic procedure is

[1] Barus, Am. J. Sci., [3] 45, 87 (1893)

[2] Arch. sci. phys. nat., 26, 136, 263 (1906); 29, 49 (1909); 30, 133 (1910).

[3] Duhem, Ann. de l'École normale sup., [3] 4, 9 (1887); Margules, Sitzungsbericht der Wiener Akademie, 104, II, 1243 (1895); Ostwald, Lehrbuch der allgemeinen Chemie, II, 2, pp. 636–640 (Ed. 2, Leipzig, 1902), Nernst, Theoretische Chemie, p. 115 (Ed. 7, Stuttgart, 1913).

selected for the present scrutiny. For the sake of shortness and simplicity, we choose the method of reversible distillation and will follow Luther's form of demonstration.[1]

Let a given binary mixture contain g_1 grams of the first component and g_2 grams of the second component, and let the corresponding partial vapor pressures be p_1 and p_2.[2] We imagine this mixture divided into two halves. Then, with the aid of a semi-permeable membrane, we transfer, by isothermal and reversible distillation, the slight quantity Δg_1 grams of the first component from the first to the second half. And next, with the aid of another semi-permeable membrane, we similarly transfer Δg_2 grams of the second component from the first to the second half of the mixture. We make $\Delta g_1/\Delta g_2 = g_1/g_2$; i. e., the small quantities transferred are in the same ratio as the total quantities of the components in the original mixture. Then the system is after the two distillations in the same state thermodynamically as before. And as the distillations were isothermal and reversible, the algebraic sum of the work involved in them must be zero: $W_1 + W_2 = 0$.

We proceed to calculate W_1 and W_2. Let, during the first distillation, the pressure p_1 of the first component in the first half of the mixture change to $p_1 - \frac{1}{2} dp_1$, and let the pressure in the second half of the mixture change from p_1 to $p_1 + \frac{1}{2} dp_1$, making a total differen of dp_1 after the first distillation. The distillation consisted, to begin with, in the reversible evaporation of Δg_1 grams; and in view of the narrow limits involved, the evaporation may be regarded as having taken place under constant pressure, namely the average pressure p_1 $\frac{1}{4} dp_1$. If we denote by v'_1 the volume of one gram of the vapor under this average pressure, then the work gained by the evaporation is $+\Delta g_1(p_1 - \frac{1}{4} dp_1)v'_1$. During the reversible condensation of the vapor in the second half of the mixture, the average pressure, likewise assumed constant, must be $p_1 + \frac{1}{4} dp_1$, and if v''_1 denotes the volume of one gram of the vapor under this pressure, then the work involved in the condensation is $-\Delta g_1(p_1 + \frac{1}{4} dp_1)v''_1$.

In order to have: $\Delta g_1(p_1 - \frac{1}{4} dp_1)v'_1 = \Delta g_1(p_1 + \frac{1}{4} dp_1)v''_1$, we must make the assumption that the product of pressure and volume is constant, but only within limits differing by $\frac{1}{2} dp_1$; further, that product need not at all equal RT/M_1 (where M_1 is the molecular weight of the component in question). All we thus assume is that, no matter what the shape of

[1] See Ostwald, *Loc cit.*, pp. 639-640.

[2] The partial pressure of each component is the pressure that would be established in a closed space separated from the vessel containing the mixture by a membrane permeable to all sorts of molecules of that component only. If the components of a binary mixture form no mixed molecular complexes, then the total pressure π is equal to the sum of the two partial pressures as just defined: $\pi = p_1 + p_2$. But the Duhem-Margules equation, generalized, applies to mixtures of any number of components, and whether association of different molecules is possible or not.

the pv curve plotted with respect to p, whether it is — in conformity with the gas laws—a straight line parallel to the p-axis, or not, *two of its ordinates separated by an indefinitely small interval are equal.*

The work W_1, then, involved in our first distillation is only that required to compress the Δg_1 grams of vapor from $p_1 - \frac{1}{4} dp_1$ to $p_1 + \frac{1}{4} dp_1$. And here again we do not use the ideal gas laws when we write: $-W_1 = -\frac{1}{2}\Delta g_1 v_1 dp_1$, where v_1 denotes the average volume of one gram within the narrow interval of pressures. Analogously, without employing the gas laws, we get for the work involved in the distillation of the second component: $+W_2 = +\frac{1}{2}\Delta g_2 v_2 dp_2$. And therefore: $\frac{1}{2}\Delta g_1 v_1 dp_1 + \frac{1}{2}\Delta g_2 v_2 dp_2 = W_1 + W_2 = 0$, or $g_1 v_1 dp_1 + g_2 v_2 dp_2 = 0$; whence: $dp_1/dp_2 = -g_2 v_2/g_1 v_1$. Substituting for v_1 and v_2 (the volumes of 1 gram) their reciprocals g'_1 and g'_2, the weights of 1 cc., we get:

$$dp_1/dp_2 = -g'_1 g_2/g_1 g'_2 \qquad (A)$$

If our original mixture is confined within a closed vessel, and an indefinitely small amount of it is allowed to evaporate, then, while g_1/g_2 represents the ratio of the weights of the two components in the liquid, g'_1/g'_2 will equal the ratio of the weights in the vapor (the two vapors being enclosed within the same space).

This expression (A) is the Duhem-Margules equation in the simplest form. The above mode of deduction frees the equation from its supposed dependence on the ideal gas laws and shows it to possess the rank of a purely thermodynamic law, from which there can be no deviation. If this were not true, then, since the behavior of vapors generally differs from that of ideal gases, dp_1/dp_2 would generally *not* be equal to $-g'_1 g_2/g_1 g'_2$. When, now, the total vapor pressure π ($= p_1 + p_2$) is a maximum or a minimum, $\delta\pi = 0$ and dp_1 must equal $-dp_2$, so that $dp_1/dp_2 = -1$. Then, (A) not being strictly true, $g'_1 g_2/g_1 g'_2$ would *not* equal 1; in other words, vapor and liquid would *not* have the same composition, and evaporation would yield fractions respectively more and less volatile than the original mixture—which is impossible, since π is a maximum or a minimum. We conclude that expression (A), the Duhem-Margules equation, must be strictly true.

If we choose to speak in terms of molar fractions, then, in order that (A) should remain true, g_1 and g'_1 must be divided by the same molecular weight M_1, and g_2 and g'_2 by the same molecular weight M_2. The molar fractions x and $1 - x$ of the liquid phase will thus be based on the same molecular weights as the molar fractions of the vapor. And if the partial pressures are taken to be proportional to the molar fractions in the vapor, which must necessarily be the case if the "molecular weights" themselves are defined on the basis of the gas laws, then expression (A) turns into the more familiar forms of the Duhem-Margules equation:

$$dp_1/dp_2 = -p_1(1 - x)/p_2 x$$

and

$$d \ln p_1/d \ln x = d \ln p_2/d \ln (1 - x).$$

Worcester, Mass.

[Contribution from the Chemical Laboratories of Clark University.]

THE LAWS OF RAOULT AND HENRY AND THE CONSTANTS OF EBULLIOSCOPY AND CRYOSCOPY.

By M. A. Rosanoff and R. A. Dunphy.

1. Introductory.

The formulae for calculating ebullioscopic and cryoscopic constants are usually deduced by combining: (1) van't Hoff's equation connecting osmotic pressure with the lowering of vapor pressure; (2) the Clapeyron-Clausius equation, together with the gas laws; and (3) Raoult's law.[1] The possibility of thus calculating constants needed in determinations of molecular weights is counted among the achievements of the theory of osmotic pressure which entitle it to its central position in theoretical chemistry.

The object of the present communication is to show that the constants in question can be found on the basis of Raoult's law and the gas laws, without the use of the osmotic pressure concept; and, on the other hand, to show that Raoult's law follows, together with the law of Henry, from the Duhem-Margules equation—a purely thermodynamic relationship. While no particular originality is claimed for our considerations,[2] it is hoped that they may be of some value, partly because of their transparency, partly on account of their bearing on the question as to the relative scientific importance of the osmotic pressure concept. Furthermore, the ebullioscopic constants calculated by us are probably more exact than those found either on the basis of the heats of vaporization (which are seldom known accurately), or by direct ebullioscopic measurement (which involves the assumption that in the cases chosen as standard the molecular weight of the solute is normal—an assumption that is seldom free from doubt).

2. Deduction of Raoult's and Henry's Laws from the Duhem-Margules Equation.[3]

To a pure solvent, whose vapor pressure in the free state is P_1, we add

[1] See Nernst, *Theoretische Chemie*, Ed. 7 (Stuttgart, 1913), pp. 148 and 283.

[2] See Arrhenius's first deduction of the ebullioscopic formula, in a letter quoted by Beckmann (*Z. physik Chem.*, 4, 550–551 (1889)), and especially Beckmann and Liesche (*Ibid.*, 86, 337 (1914)). *The subject matter of this present communication was in the main ready for publication in January,* 1913; the ebullioscopic constants have recently been recalculated.

[3] A somewhat complicated deduction of Raoult's law (but not of Henry's) was given by Story (*Phil. Mag.*, [6] 20, 97 (1910)).

an infinitesimal amount of some second substance. The molar fraction of the solvent becomes x (still very nearly 1); that of the solute, $(1 - x)$, is now identically equal to $d(1 - x)$. The partial vapor pressure of the solute, p_2, is identically equal to dp_2. Thus $dp_2/p_2 = d \ln p_2 \equiv 1$ and $d(1 - x)/(1 - x) = d \ln (1 - x) \equiv 1$, and therefore $d \ln p_2/d \ln (1 - x) \equiv 1$. But according to the Duhem-Margules equation·
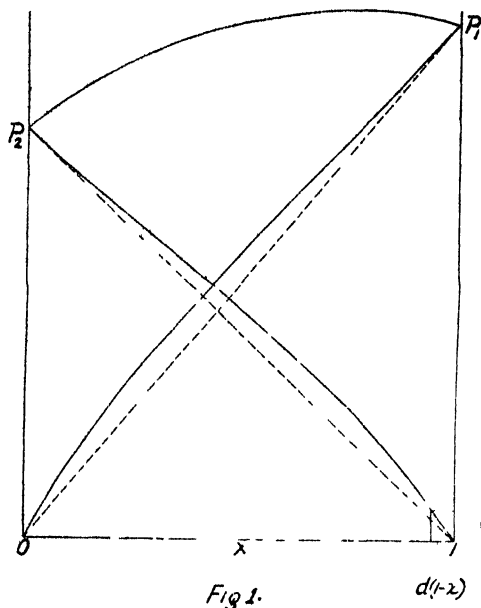
$$d \ln p_1/d \ln x = d \ln p_2/d \ln (1 - x)$$

It follows that at the very great dilution which we are considering $d \ln p_1/d \ln x = 1$, whence $dp_1/dx = p_1/x$ and, as at our dilution $x = 1$ and $p_1 = P_1$, we find.

$$dp_1/dx = P_1,$$

which is Raoult's law.

Fig 1.

Experimentally, Raoult's law holds true generally not only at infinite dilution (*i. e.*, at $x = 1$), but up to concentrations of *at least* 5 molar per cent. (*i. e.*, between $x = 1$ and $x = 0.95$). Within these limits the slope of, the curve representing the partial pressures of the solvent remains constant and equal to P_1; in other words, within these fairly wide limits the partial pressure curve is coincident with the straight line connecting the points $x = 0$ and $p_1 = P_1$. Since, thus, $d \ln p_1/d \ln x$ remains equal to unity, the Duhem-Margules equation teaches that also

$$d \ln p_2/d \ln (1 - x) = 1.$$

Integrating this within the permissible limits, we get:

$$p_2 = k(1 - x),$$

where k is an integration constant.[1] But *this last equation expresses nothing else than Henry's law:* that the solubility of a gas or vapor is proportional to the pressure. Only, as the equation shows, the "solbility" must be measured in terms of the molar fraction of the solute.

Raoult's and Henry's laws are thus intimately connected through the

[1] In certain cases, though not frequently, $k = P_2$, which is the vapor pressure of the solute in the isolated state

Duhem-Margules equation, and each law is seen to hold to the same limits of concentration as the other.

3. Ebullioscopic Constants.

To 100 g. of a solvent, the molecular weight of whose vapor at the boiling point T is M_o, and whose vapor pressure at the same temperature is P_1, we add Δ grams of a substance of molecular weight M. The result is a depression of P_1, to the smaller value p_1. On the other hand, we cool a quantity of the pure solvent to a temperature, say, t degrees below its boiling point, so that its vapor pressure P_1 is lowered again to the value p_1. We now *assume* that, if we should raise both the temperature T of our solution and the temperature $T - t$ of the solvent t degrees, their lowered vapor pressures p_1 would rise back to one and the same value P_1. By making this assumption we commit an error. For the rise of the partial pressure of the solvent *in the solution* between T and $T + t$ will *not* generally be the same as the rise of the vapor pressure of the pure solvent between the temperatures $T - t$ and T. If, however, the amount Δ grams of solute in our solution is infinitely small, then the properties of solution and solvent approach identity, and the error involved in our assumption becomes infinitely small.

Under these conditions, then, no error is really committed by equating the rise of vapor pressure per degree in the solution and the rise of vapor pressure per degree in the pure solvent $(P_1 - p_1)/t = dP_1/dT$. From this we have

$$t = (P_1 - p_1)dT/dP_1 \qquad (1)$$

We now introduce Raoult's law, in the form $p_1 = P_1 x$, or rather in the form $P_1 - p_1 = P_1(1 - x)$. The symbol x represents the molar fraction of the solvent in the solution:

$$x = \frac{100/M_o}{100/M_o + \Delta/M}$$

Equation (1) now becomes·

$$t = P_1(1 - x)dT/dP_1 =$$
$$P_1\Big(1 - \frac{100/M_o}{100/M_o + \Delta/M}\Big)\frac{dT}{dP_1} = P_1\Big(\frac{\Delta/M}{100/M_o + \Delta/M}\Big)\frac{dT}{dP_1}$$

Since Δ is infinitely small, we may write.

$$t = \frac{P_1\Delta/M}{(100/M_o)(dP_1/dT)};$$

and as t is the elevation of the boiling point caused by the addition of Δ/M mols of the solute, E, the elevation per *one* mol of solute, is

$$E = \frac{P_1}{(100/M_o)(dP_1/dT)}.$$

The molecular weight M_o of the vapor of the solvent is found by determining the specific volume of the vapor and applying the gas laws (which

are perfectly reliable for the pressures of an ordinary boiling-point determination): $M_0 = RT/P_1 v$. Therefore, finally:

$$E = \frac{RT}{100 \, v dP_1/dT} \tag{2}$$

That both the specific volume of the vapor at the boiling point and the variation of vapor pressure with the temperature, needed in Formula 2, can be measured with considerable accuracy, is indicated by many data in the literature; not only do the measurements of one and the same observer usually appear consistent among themselves, but the measurements of different investigators, carried out at different periods, are often in excellent agreement. For instance, according to Wüllner and Grotrian, the specific volume of chloroform vapor is 0.226 liters; according to Young it is 0.229 liters. Again, according to Young (1889) the vapor pressure of benzene between 70° and 80° increases by 20.62 millimeters for each degree, while according to Smith and Menzies (1910) the increase is 20.65 mm.; between 80° and 90°: 25.25 (Young) and 25.05 (Smith and Menzies); between 90° and 100°: 32.8 (Young) and 33.0 (Smith and Menzies); between 100° and 110°: 40.4 (Young) and 40.3 (Smith and Menzies); between 110° and 120°: 49.0 (Young) and 48.9 (Smith and Menzies). Similarly, values of E for acetic acid calculated by Equation 2 from the pressure measurements of Landolt (1868), Ramsay and Young (1886), Kahlbaum (1894), and the data given by Young in his paper of 1910, vary only between 32.4 and 33.4. On the other hand, the figures found by direct ebullioscopic measurement vary between 25.4 and 30.7, and the figures calculated from the heat of vaporization vary between 29.8 and 35.7.

The figures given in Table I were obtained by plotting the latest available measurements on a sufficiently large scale and "smoothing" the curves, —which yielded somewhat more precise results than would have been found by linear interpolation. In all cases, to attain greater reliability, the E's were calculated for the atmospheric pressures 730, 760 and 780 mm., and plotted with respect to these pressures; then a straight line was drawn as nearly as possible to the three points, and the E's read off from the line. The table gives in each case the value of E thus obtained for 760 mm. and, in the last column, the correction to be added for every 10 mm. between 760 and 780 mm., or subtracted for every 10 mm. between 760 and 730 mm. We are inclined to believe that most of these ebullioscopic constants are within, say, 2% of the true values.

TABLE I.—EBULLIOSCOPIC CONSTANTS.

No.	Solvent.	Boiling point under 760 mm.	dP_1/dT (atm).	v (liters).	E (760 mm.).	Correction per 10 mm.
1	Acetic acid...	118.51°	0.0308	0.318	32.8	0.08
2	Benzene	80.15	0.0309	0.364	25.8	0.24
3	Bromobenzene........	155.83	0.0251	0.211	66.5	0.60
4	Carbon disulfide.......	46.00	0.0325	0.335	24.0	0.20

TABLE I (*continued*)

No	Solvent.	Boiling point under 760 mm	dP_1/dT (atm)	v (liters)	E (760 mm)	Correction per 100 mm
5	Chlorobenzene	131 98	0 0271	0 282	43 5	0 24
6	Chloroform	60 19	0 0329	0 229	36 4	0 10
7	Cyclohexane	80 88	0 0301	0 337	28 7	0 11
8	Di isobutyl	109 26	0 0282	0 162	68 9	0 38
9	Di-isopropyl	58 10	0 0320	0 304	28 0	0 14
10	Ethyl alcohol	78 26	0 0379	0 613	12 4	0 10
11	Ethyl ether	34 42	0 0358	0 320	22 1	0 07
12	Ethyl formate	54 48	0 0347	0 353	21 9	0 06
13	Ethyl acetate	77 13	0 0317	0 313	29 0	0 12
14	Ethyl propionate	99 01	0 0312	0 287	34 1	0 20
15	Fluorobenzene	85 41	0 0301	0 295	33 1	0 22
16	Heptane (normal)	98 42	0 0292	0 292	35 8	0 22
17	Hexane (normal)	68 59	0 0313	0 310	28 9	0 07
18	Iodobenzene	188 47	0 0239	0 175	90 7	0 42
19	Methyl alcohol	64 67	0 0399	0 829	8 4	0 09
20	Methyl formate	31 92	0 0377	0 408	16 3	0 10
21	Methyl acetate	57 11	0 0345	0 357	22 0	0 09
22	Methyl propionate	79 59	0 0330	0 316	27 7	0 16
23	Methyl butyrate	102 62	0 0309	0 282	35 4	0 18
24	Methyl isobutyrate	92 48	0 0297	0 277	36 4	0 16
25	Octane (normal)	125 80	0 0284	0 264	43 7	0 05
26	Pentane (normal)	35 98	0 0354	0 336	21 3	0 12
27	Pentane (iso)	28 02	0 0365	0 326	20 8(?)	
28	Propyl alcohol	97 14	0 0365	0 489	17 1	0 12
29	Propyl formate	81 20	0 0325	0 317	28 3	0 08
30	Propyl acetate	101 68	0 0299	0 286	36 1	0 10
31	Stannic chloride	114 20	0 0263	0 117	103 2	1 0
32	Water	100	0 0358	1 651	5 18	0 07
33	Carbon tetrachloride*	76 50	0 0314	0 181	50 5	0 36

The pressure and temperature values used in calculating this table are based on the following measurements

For (1) Ramsay and Young *J Chem Soc*, **59**, 903 (1891)

For (2) Smith and Menzies *J Am Chem Soc* **32**, 1453 (1910)

For (3) (5), (15) and (18), Young *J Chem Soc*, **55**, 486 (1889)

For (4) Battelli, *Mém Accad Torino* **41**, I (1890) **42**, I (1891)

For (6) Regnault, *Mem de l Acad* **26**, 339 (1862)

For (7) (12) (20), (27) and (33) Young *Sc Proc R Dublin Soc* [N S] **12**, 374 (1910)

For (8) and (9) Young and Fortey, *J Chem Soc*, **77**, 1126 (1900)

For (10) Ramsay and Young, *Phil Trans*, **177**, I, 123 (1886)

For (11) and (19) Ramsay and Young, *Phil Trans* **178A**, 57 (1887)

For (13), (14), (21), (22), (23) (24) (29) and (30) Young and Thomas, *J Chem Soc*, **63**, 1191 (1893)

For (16) Young, *Ibid*, **73**, 675 (1898)

For (17) Young and Thomas, *Ibid*, **67**, 1075 (1895)

For (25) Young, *Ibid*, **77**, 1145 (1900)

For (26) Young, *Ibid*, **71**, 446 (1897)

* Added in proof

For (28) Ramsay and Young, *Phil. Trans.*, 180, 137 (1889).

For (31) Young, *Phil. Mag.*, [5] 34, 512 (1892)

For (32) Regnault (recalculated by Broch), Landolt-Bornstein, *Tabellen* (Ed 4, Berlin, 1912, pp 366–367).

The specific volumes used in the table are based on the following data:

For (1), (2), (3), (5), (7), (8), (9), etc., to (31), and (33) Young, *Sc Proc R. Dublin Soc.*, [N S] 12, 374 (1910)

For (4) and (6) Wullner and Grotrian, *Wied Ann*, 11, 556 (1880)

For (32) Zeuner, see Landolt-Börnstein, *Tabellen* (Ed 4, Berlin, 1912, p 369)

4. On Measurement of the Lowering of Vapor Pressure with the Aid of a Beckmann Ebullioscope.

It may be of interest to record here that a Beckmann ebullioscope, connected with an empty tank by *sufficiently wide tubing*, can be used for determining the lowering of vapor pressures at constant temperature. In making the measurements tabulated below, we used tubing of 1 cm. internal diameter and a tank of 100 liters capacity. No other "manostat" was necessary.[1] The pressures, which were considerably below that of the atmosphere, were measured with the aid of a baromanometer with a mirror scale. Kahlbaum's thiophene-free benzene was used as a solvent. Our naphthalene had been twice sublimed, twice recrystallized from alcohol, washed with water, and dried over phosphorus pentoxide. The anthracene had been similarly purified by repeated sublimations and repeated recrystallizations from alcohol The molecular weights were calculated by the formula:

$$M = M_0(g/G)[p_1/(P_1 - p_1)],$$

where the symbols M, M_0, P_1, and p_1 have the same meaning as in the preceding section; G and g are the weights of solvent and solute, respectively. Here the variation of the vapor pressure of the solvent with the temperature is not needed, and thus one source of error is eliminated.

In the practice of the organic laboratory, M_0 may in the case of all "unassociated" solvents be assumed equal to the normal molecular weight. That the results are as good as those usually obtained from elevations of the boiling point under constant atmospheric pressure, is indicated by the following measurements:

1 *Determination of the Molecular Weight of Naphthalene in Benzene* —Weight G of benzene taken = 26 53 g The observed pressure P_1 of the pure solvent was 639 85 mm The molecular weight of benzene vapor, M_0, assumed = 78.1 Found

g.	p_1 mm.	M.
0 7913	628 7	131 3
1 3141	621 6	131 7
1 8411	614 5	131 3
2 3446	607 4	129 2
3 3453	594 3	128 5

The normal molecular weight of naphthalene is 128 06.

[1] See Beckmann, *Z. physik. Chem*, 79, 565 (1912)

2 Determination of the Molecular Weight of Anthracene in Benzene —Weight G of anthracene taken $= 29\,740$ g   The observed pressure P_1 of the pure solvent was $639\,7$ mm   The molecular weight of benzene vapor, M_0, assumed $= 78\,1$ Found.

g.	p_1 mm	*M.*
0 5676	634 6	185 4
0 8696	631 9	184 8

The normal molecular weight of anthracene is 178 08

5. Cryoscopic Constants.

Let the straight lines in Fig 2, marked "Ice," "Water," and "Solution," represent the tangents to the corresponding vapor-pressure curves at the

points P_1, again P_1, and p_1, respectively. If the solution under consideration is infinitely dilute, then the points P_1, p_1, and p , are infinitely near together, and the tangents may be considered in place of the vapor-pressure curves themselves, without any finite error being committed.

Fig 2.
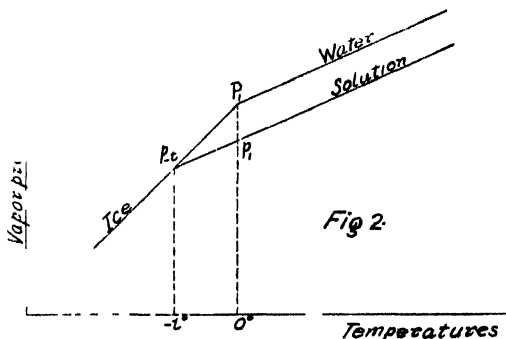
What is sought is the depression t of the freezing point, caused by the addition to 100 g. of the solvent, the molecular weight of whose vapor may be M_0, of an infinitely small quantity Δ grams, or Δ/M mols, of solute.   Geometrically, what is sought is the t corresponding to the point of intersection of the ice and solution lines.   The ice line passes through P_1, which represents the vapor pressure of the solvent at the freezing point; and its slope may be denoted by $\partial p_i/\partial t$ (the subscript i referring to ice). The equation of the ice line is therefore.

$$p = P_1 + (\partial p_i/\partial t).t \qquad (3)$$

The solution line passes through the point p_1, which represents the vapor pressure of the solution at the freezing temperature of the solvent.   The slope of this line is the same as that of the water line, since the solution is infinitely dilute (see section 3 above).   It may be denoted by $\partial p_w/\partial t$ (the subscript w referring to water, the pure solvent).   Then the equation of the solution line is:

$$p_s = p_1 + (\partial p_w/\partial t).t \qquad (4)$$

At the freezing point of the solution $p_i = p_s = p_{-t}$.   Hence, from (3) and (4):

$$P_1 + (\partial p_i/\partial t).t = p_1 + (\partial p_w/\partial t).t$$

and

$$t = -\frac{P_1 - p_1}{\partial p_t/\partial t - \partial p_w/\partial t}. \tag{5}$$

Now we apply Raoult's law and, accordingly, substitute for $P_1 - p_1$ its equal $P_1(1 - x)$, as in section 3. Remembering further, that x, the molar fraction of the solvent, is

$$x = \frac{100/M_0}{100/M_0 + \Delta/M},$$

and that the solution is infinitely dilute, equation (5) becomes:

$$t = -\frac{P_1\Delta/M}{(100/M_0)(\partial p_t/\partial t - \partial p_w/\partial t)}$$

Finally, since $M_0 = RT/P_1v$, where v is the specific volume of the vapor of the solvent, the depression E per *one* mol of solute becomes:

$$E = -\frac{RT}{100\ v(\partial p_t/\partial t - \partial p_w/\partial t)} \tag{6}$$

Unlike the corresponding expression for the molecular elevation of the boiling point, this expression (6) for the constant of cryoscopy has scarcely more than theoretical interest; for the *difference* of the two slopes involved is usually small and difficult to determine with precision. Here van't Hoff's formula, based on the heat of fusion of the solvent, will usually be of greater practical advantage. Both expressions (2) and (6) turn into the commonly used Van't Hoff formulae if combined with the Clapeyron-Clausius equation; for ebullioscopic purposes, as we have seen, this transformation is not desirable.

In conclusion we would point out that, since Raoult's law follows from the Duhem-Margules equation, and since the molar fractions in the latter are based on the molecular weights, not in the *liquid* mixture, but in the *vapors* emitted by it—the curious idea suggests itself that all ebullioscopic and cryoscopic measurements indicate molecular weights, not really of the substances in solution, but of their *vapors* emitted by the solution. That the molecular weight of the "solvent" in Raoult's law is that of the solvent's vapor, is generally recognized.

WORCESTER, MASS.

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS. PART II.

BY H. C. HOLDEN AND C. JAMES
Received May 13, 1914

In a previous paper, the authors have shown several methods of separating yttrium from the yttrium earths, the most efficient of which were, the fractional precipitation of the chromates and the fractional precipi-

tation of the phosphates. These methods, however, were not well adapted to the separation of yttrium on a commercial scale, and therefore the work was continued in hope of finding a suitable method to use in working up large quantities of material.

A. Fractional Precipitation by Means of Sodium Nitrite.

The material first used was the most soluble portion obtained during the fractionation of the yttrium earths from Carolina monazite by the bromate method. It contained ytterbium, lutecium, erbium, thulium and yttrium with traces of thorium. A quantity of this material was converted into the oxide dissolved in nitric acid and diluted to about 1500 cc. with water. This was boiled and stirred by means of steam, while an amount of a concentrated solution of sodium nitrite was added sufficient to precipitate about one-third the rare earth material present. In a like manner, another precipitate was obtained from the mother liquor. Nitric acid was then added to the filtrate from Fraction 2 in order to liberate the nitrous acid and Fraction 3 was obtained by means of oxalic acid. These fractions were then purified by reprecipitating as oxalates, igniting, boiling the oxides with water to free them from sodium, dissolving in hydrochloric acid, reprecipitating as oxalate and igniting. A portion of each was then taken and the equivalent determined by the method described in Part I.

SUMMARY

No. of fraction.	Atomic weight
1	117.2
2	95.9
3	91 4

Fraction I was then dissolved in nitric acid and diluted to about 750 cc. with water, a small quantity of sodium nitrite was added and the solution placed in a flask, where the pressure was reduced considerably at room temperature. In this manner Fraction 1A was obtained and proved to be thorium. The mother liquor was then fractionated further by means of sodium nitrite. The method was similar to that used in the first case, except that a smaller quantity of sodium nitrite was added each time. Five fractions were thus obtained, and, after purification, the equivalents were determined.

SUMMARY.

No. of fraction.	Atomic weight
1A	Thorium
1B	148.50
1C	136.25
1D	124.60
1E	110.20
1F	95.20

Fraction 1B was nearly rose color and gave a fairly dense oxalate. Frac-

tien. 1C was a light pink color and gave an oxalate less dense than 1B. 1D was more pink than 1C and also denser. 1E was lighter in color than 1D but was about the same density. Fraction 1F was lighter colored than 1E and gave a very fluffy oxalate.

Fraction 2 was then dissolved in nitric acid and diluted to about 700 cc. with water, boiled and stirred as before. By adding a sufficient amount of sodium nitrite to precipitate about one-fourth the rare earth material present, Fraction 2A was obtained. In the same way, three more fractions were obtained and then nitric acid was added to free the solution of nitrous acid, after which oxalic acid was added to get Fraction 2E. These were then purified and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight
2A............................	111.00
2B............................	105.30
2C............................	104.50
2D............................	96.40
2E............................	91.00

Fraction 2A was pink and fairly dense, the color of the series gradually grew lighter to 2E, which was just slightly pink. The poor separation between 2B and 2C was due to the fact that the precipitate was colloidal and not granular as the others.

Fraction 3 was next dissolved in nitric acid, diluted to about 700 cc. with water and four fractions obtained in a similar manner to that in the previous case. These were purified as before and the equivalents determined.

SUMMARY.

No. of fraction	Atomic weight
3A.	94.00
3B............................	91.10
3C............................	89.50
3D..........	. .

Fraction 3A was similar in color to Fraction 2C and was fairly dense. 3B was nearly white with about the same density as 3A. 3C was white with a tinge of yellow. 3D had a tendency toward pale buff and there was not a sufficient quantity to make an equivalent determination. Fractions 3A, 3B, and 3C were about of equal size. By means of the spectrograph it was found that 1B gave an intense ytterbium spectrum while 1D contained no ytterbium. Fraction 3C consisted of practically pure yttrium. This can be seen to be the most efficient and rapid method of separation found up to the present time.

Since the separation of yttrium from dysprosium and holmium is more difficult than from erbium, it was thought that it would be of interest to apply the nitrite method to a mixture of yttrium, dysprosium, and holmium,

containing traces of terbium and neodymium.   About 50 g. of these oxides were dissolved in nitric acid and diluted to 800 cc. with water.   The method of fractionation was the same as in the previous case, except that a large excess of sodium nitrite was added at the very beginning of the fractionation.   The first three fractions obtained were very markedly colloidal and could not be filtered, but had to be allowed to stand over night to settle.   The final fraction was taken by means of oxalic acid after freeing from the nitrous acid.   The fractions were then purified and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.
1	117 80
2	115 90.
3	115 70
4	114.90

The fact that the separation was very inefficient was probably due to the colloidal condition of the precipitate obtained.   After a careful investigation of the variables involved in the fractionation, it was found that a very large excess of sodium nitrite would cause the precipitate to be colloidal instead of granular.   Therefore, the same material was taken and subjected to fractionation again, care being taken to avoid an excess of sodium nitrite.   Eight fractions were thus obtained, the last one being precipitated with oxalic acid.   It took considerable boiling to obtain the fractions and the precipitate was very fine and filtered readily.   Terbium was found to collect in the first fractions, while neodymium was concentrated in the last fraction and was removed by means of sodium sulfate.   These various fractions were then purified as before and their equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.
1	121.10
2	120.80
3	117.60
4	116.70
5	113.60
6	112.10
7	107.50
8	99.40

A mixture of the oxides of yttrium and erbium was dissolved in nitric acid, diluted to about one liter and subjected to the same method of fractionation.   In the first case, five fractions were obtained by using a large excess of nitrite.   The somewhat colloidal precipitates were purified as before and as there was no apparent separation when examined by the spectroscope, the equivalents were not determined.

The same material was taken and fractionated again, with only a slight

excess of sodium nitrite over the amount required to precipitate the first fraction. Six fractions were obtained, all of which were crystalline and filtered rapidly. These were purified and their equivalents determined as before. A gradual change of color could be seen in going from Fraction 1, which was pink, to Fraction 6, which was pure white.

<div align="center">

SUMMARY.

No. of fraction.	Atomic weight.
1	92.5
2	90.9
3	90.7
4	90.2
5	90.0
6	88.3

</div>

By this method about 20% of the original material was obtained in the last fraction, which was pure yttrium.

Fractionation of Gadolinite Material. — About 300 g. of rare earth oxides, obtained from gadolinite, were dissolved in nitric acid and diluted to about three liters with water. This was boiled in an enamel pail and sodium nitrite added in small amounts until a fair sized precipitate was formed. In this way eight fractions were obtained. The first and second precipitates were somewhat gelatinous, but the succeeding ones grew more granular and filtered readily. Upon examination, the first fraction was found to contain thorium. Fraction 2 showed a strong spectrum of erbium. Fraction 3 gave a strong erbium spectrum and a trace of neodymium. Fraction 4 showed a decrease in the erbium spectrum and a trace of neodymium. Fraction 5 gave a further decrease in the erbium with an increase in the neodymium. Fraction 6 showed an increase in the neodymium and a trace of erbium. In Fraction 7 a still further increase in the neodymium and a trace of erbium were apparent. Fraction 8 gave an increase in the neodymium and no erbium whatsoever. The last three fractions contained about one-fifth the original material. From these results it would seem that the yttrium could be separated from the gadolinite earths very rapidly.

B. Fusion of the Nitrates.

A mixture of erbium and yttrium oxides were dissolved in nitric acid and the resulting nitrates evaporated and fused until brown fumes began to be evolved. This fused mass was then poured into a casserole containing cold water and then dissolved by heating and evaporated just a slight amount. The basic nitrates were then allowed to crystallize out by standing over night. The crystals thus obtained formed Fraction 1 and the filtrate was submitted to the same treatment as before to obtain Fraction 2. In this way six fractions were obtained. Fraction 7 was precipitated from the filtrate of Fraction 6 by means of oxalic acid and contained about one-fourth the original material.

SUMMARY.

No. of fraction.	Atomic weight.
1	90 80
2	91.25
3	90.85
4	89.65
5	88.80
6	88.45
7	88.00

As can be seen, Fraction 1 gave an atomic weight less than Fraction 2. This was due to the fact that the decomposition was carried too far and therefore the basic nitrate obtained was somewhat colloidal and also the fused nitrate was not entirely soluble in water.

C. Fractionation by Means of Boiling with Sodium Hydroxide.

A concentrated nitrate solution containing yttrium and erbium was boiled, and a sufficient quantity of sodium hydroxide added to precipitate about one-fifth the rare earth material present. This was boiled for a short time and then allowed to stand over night in order that the basic nitrate might crystallize out. In this way three fractions were obtained and the fourth precipitated with oxalic acid. These were purified as before and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.
1	90.30
2	89.90
3	88.75
4	88.30

Conclusions.

The best method found thus far for separating yttrium efficiently from the other earths is by means of fractional precipitation with sodium nitrite. This gives a larger yield, a more rapid separation and is less expensive than either the phosphate or chromate method. This method is, however, not very effective for separating terbium from yttrium.

CONTRIBUTION TO THE CHEMISTRY OF GOLD. II. AUTO-REDUCTION AS A FACTOR IN THE PRECIPITATION OF METALLIC GOLD.

By Victor Lenher.

In the various studies which have been made on the precipitation of gold from solution, attention has been directed for the most part to the action of various *reducing* agents on gold solutions. The general chemical inactivity of gold enables us to deposit the metal in elementary form by most of the metals, the metallic sulfides, ferrous salts, various organic com-

pounds, and, in fact, in the ordinary sense of the word, gold compounds are readily reduced to metal by the mildest of reducing agents.

On the other hand, very little attention has been directed to the precipitation of gold in the metallic condition by oxidizing agents. A few isolated cases of the "auto-reduction" of gold from its compounds by certain oxidizing agents have been recorded, but the general principle of the auto-reduction of gold compounds has not received systematic study from the standpoint of the deposition of gold.

It has been known for a long time that hydrogen peroxide, when brought in contact with oxide of gold or oxide of silver, will reduce either of these metallic oxides to metal, water and oxygen being formed simultaneously.

$$Au_2O_3 + 3H_2O_2 = 2Au + 3H_2O + 3O_2.$$
$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$
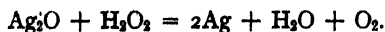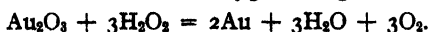
In a similar manner, gold solutions in contact with hydrogen peroxide yield metallic gold, oxygen being evolved at the same time. This reaction of hydrogen peroxide with gold compounds takes place in either acid or alkaline solution. Sodium peroxide and sodium perborate precipitate metallic gold immediately from gold solutions. Barium peroxide and calcium peroxide act toward gold solutions in exactly the same way, precipitating metallic gold at once. These compounds are perhaps closely related to hydrogen peroxide and, as a consequence, act similarly toward gold solutions. Osmium tetroxide, or the so-called osmic acid (OsO_4), when dissolved in water will not reduce gold solutions, but when the free acid is neutralized, or when the solution is made alkaline with sodium hydroxide, sodium carbonate or calcium carbonate, metallic gold is precipitated. The higher oxides of nickel and cobalt, prepared by the action of an alkaline hypobromite on solutions of nickel and cobalt chloride, when brought in contact with a solution of gold which has been rendered alkaline, precipitate metallic gold.

Lead peroxide as well as red lead precipitate metallic gold from either neutral or alkaline gold solutions.

Ceric oxide, prepared in the hydrated form by rendering ceric chloride alkaline, precipitates metallic gold at once from a gold solution which has been rendered alkaline.

The compounds of manganese present interesting deportment along this same general line of auto-reduction. Manganese dioxide, prepared by the action of bromine on a manganese acetate solution, precipitates gold from its solution either under slightly acid, neutral, or alkaline conditions. Potassium permanganate, on being allowed to stand for some time with auric chloride, causes metallic gold to be precipitated along with manganese dioxide.

The minerals pyrolusite, wad, braunite and manganite, when brought

in contact with a gold solution, which is either acid, alkaline, or neutral, slowly cause gold to deposit.

Recently Brokaw[1] has shown that manganese salts, when made alkaline, or even manganese carbonate will precipitate gold from solution. The direction of the reaction between manganous salts and gold chloride is considered by Brokaw to be largely due to hydrolysis of gold chloride solutions, although the equations, as given, show that gold chloride and manganous salts react in neutral solution to form manganese dioxide and metallic gold. All of the reactions recorded by Brokaw have been studied and corroborated. That manganese can be of considerable importance in the deposition of gold is unquestionably true, and its function may be that which Brokaw has suggested; but, in addition, manganese may play the role of a reducing agent, acting solely through auto-reduction.

Auric compounds, as is well known, are easily reduced to metallic gold, and, hence, can be considered as oxidizing agents and can, obviously, oxidize manganous hydroxide to manganese dioxide. It can therefore be considered that the mutual precipitation of gold and manganese dioxide by calcite, as cited by Brokaw, is simply the neutralization of the excess of acid, whereupon the oxidation of the manganese by the gold solution results in the precipitation of both manganese dioxide and metallic gold.

That this is the direction of the reaction is evidenced by the duplication of the phenomenon by replacing manganese salts with cerium compounds. Cerous hydroxide precipitates metallic gold in alkaline solution; the cerium being at the same time oxidized to cerium dioxide. Similarly, when a piece of calcite is introduced into a solution of cerium chloride and gold chloride, as the free acid is neutralized by the calcium carbonate a deposit of cerium dioxide containing metallic gold begins to form on the calcite.

The presence of gold in the manganese deposits, which observation has been studied by Emmons,' may be due to the fact that manganese is a significant agent in the superficial transportation of gold; but such is by no means necessarily the case. Two distinctly different kinds of reactions may be going on. In one case a chloride solution, containing free acid on coming in contact with an oxidized manganese deposit will produce free chlorine, or its equivalent. This chlorine solution can then dissolve gold and cause the production of a gold bearing manganese solution, which, so long as it contains considerable free acid, is quite permanent; but, when, it comes in contact with any neutralizing agency, for example, a limestone metallic gold and manganese dioxide would be at once precipitated. This accords with experiments which have been reproduced in the laboratory, and which do not, as indicated by Emmons, require such a reducing agent

[1] *J. Eng. Ind. Chem.*, **5**, 560 (1913).

[2] Emmons, *Trans. Am. Inst. Min. Eng.*, **1910**, 768.

as ferrous sulfate or other reducing agents as indicated by Wells,[1] to produce a precipitate. On the other hand, the gold present in the manganese deposits adjacent to other gold deposits may be due wholly to the fact that gold solutions in contact with manganese dioxide yield metallic gold, by virtue of the principle of auto-reduction shown by other peroxides with gold solutions.

The auto-reduction of gold solutions to metallic gold has apparently, thus far, not been considered as an important geological factor in the secondary deposition of gold, but it is doubtless possible that in many instances one can conceive of the oxygen of the air as being the real agent which causes the gold to be reduced in presence of a manganese or similar compound which acts as a catalytic agent.

UNIVERSITY OF WISCONSIN,
MADISON, WIS

THE VOLUMETRIC DETERMINATION OF TITANIUM AND CHROMIUM BY MEANS OF A MODIFIED REDUCTOR.

BY C. VAN BRUNT.

Shimer and Shimer[2] have described a modification of the method of Newton[3] for the determination of titanium, in which the reduction by boiling with zinc in a flask is supplanted by the use of a Jones reductor. The authors found that the ordinary form of this familiar apparatus, as used in the determination of iron, does not give complete reduction—a fact which the present writer can corroborate. They accordingly substituted a much longer and narrower tube, which modification had the desired effect.

The proposed method seemed to offer a way of escape from the tedious methods in vogue. These must include the original Newton method which, though for most purposes preferable to the gravimetric, is still lacking, mainly because of the slow disappearance of the last portions of the zinc, and the difficulty of preventing, with certainty, during this stage, the partial reoxidation of the very sensitive hot titanous solution.

But in practice in this laboratory, the Shimer reductor filled with 20-mesh zinc has been found to offer little, if any, advantage in point of time, because of the extremely slow passage of the solution through the long, thin tube. The difficulty of preventing reoxidation was present here also.

This latter point, however, was successfully met by the simple device of letting the titanous solution run directly from the reductor into an excess of ferric solution previously placed in the receiving vessel. An ex-

[1] Trans. Am. Inst. Min. Eng., 1910, 793.

[2] Orig. Comm. 8th Intern. Congr. Appl. Chem., 1, 445.

[3] Am. J. Sci., [4] 25, 130, 343.

tension tube reaching nearly to the bottom of the receiver was used. The reduction of the Fe^{III} by the Ti^{III} is instantaneous and in place of titanous sulfate only the very stable ferrous sulfate comes into contact with the atmosphere.

The slowness and inconvenience of the long, narrow reductor still remained.

The zinc used was somewhat finer than is recommended by Shimer and Shimer, and to this may be due part of the difficulty, but none other being at hand, it was sought to improve matters by using a reductor of ordinary dimensions which could be heated continuously by means of a current of electricity circulated through a winding about the barrel of the instrument. This device proved entirely successful, not only titanic but also chromic salts being completely reduced in a few minutes.

The instrument is a reductor of the usual form, having a column 2.5 cm. in diameter by 20 cm. in height of coarse granulated zinc well amalgamated. The tube is wrapped with a few feet of resistance ribbon—iron wire would suffice—in series with a lamp or other resistance adapted to taking sufficient current from a lighting circuit to boil the contained solution.

To use the reductor, the stopcock at the bottom is closed, and the tube is partly filled with hot 5% H_2SO_4, which is followed by the solution to be reduced. A 2-holed rubber stopper, carrying a funnel tube with a stopcock and a small vent tube, is then placed in the top of the reductor and the contents are brought near to boiling and held there for 10–20 minutes. The internal pressure is then, by an obvious manipulation of the openings, allowed to force the charge into an excess of acidified ferric ammonium sulfate solution through a tube extending to the bottom of the vessel as before described. A tall narrow beaker may advantageously be used. More acid is then admitted and forced out as before. These operations are carried out without access of air to the space above the zinc. The washing is then completed with 1% H_2SO_4, with the top of the reductor open as usual. The reduced iron is titrated with $KMnO_4$ in the usual manner, and the titanium present calculated:

$$Fe^{III} + Ti^{III} = Fe^{II} + Ti^{IV}$$
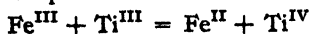
The only thing to be guarded against is a tendency for a portion of the contents of the receiver to be sucked back into the reductor if the steam in the latter is allowed to condense during emptying. This offers no practical difficulty.

The solutions for reduction should contain about 5% free H_2SO_4. Much more than this causes too vigorous action.

The procedure for chromium solutions is identical with the above:

$$Fe^{III} + Cr^{II} = Fe^{II} + Cr^{III}$$
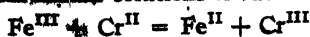
The method was checked up in the case of titanium by means of a standard solution prepared from potassium fluotitanate, K_2TiF_6, by fuming off with H_2SO_4. The TiO_2 content was determined gravimetrically by precipitation with NH_4OH with the precautions laid down by Bornemann and Shirmeister,[1] with the following results:

G. TiO_2 per cc. 0.01196, 0.01197, 0.01196

10 cc. portions of this solution were then reduced and determined as described in the foregoing, giving

G. TiO_2 per cc., 0.01196, 0.01195, 0 01195.

The permanganate solution used was standardized against Mohr's salt

For chromium, the standard solution was prepared by dissolving a weighed portion of pure fused $K_2Cr_2O_7$ and making up to a definite volume such that 1 cc contained the equivalent of 0.01035 g Cr_2O_3. This solution, analyzed by the reductor method in 10 cc portions gave

G. Cr_2O_3 per cc , 0 01032, 0 01035, 0 01035

The application of this method to the analysis of a mixture containing iron, chromium and titanium may be considered as an illustration.

The substance is brought into sulfate solution by known methods and made up to a definite volume. Iron is determined in an aliquot portion by titration after reduction in a reductor in the ordinary manner, with the important exception that Bi_2O_3 is added to reoxidize any reduced titanium and chromium.[2] Or the reduction may be effected with H_2S or SO_2 which have no action on Ti^{IV} or Cr^{III}.

A second portion is treated in the heated reductor in the manner described. The subsequent titration gives the permanganate equivalent of all three constituents combined.

The chromium alone is determined in a third portion by conversion to Cr^{VI} by boiling with ammonium persulfate and titrating in the usual manner with Fe^{II} and $KMnO_4$. Substituting the $KMnO_4$ equivalent for the Cr found, and adding to it that of the Fe, the Ti is then obtained by difference. Since the determinations upon which rests the result so obtained are not subject to significant error, the usual criticism of results by difference applies with a minimum of force, especially when one considers the well known difficulty of the separations involved in a direct determination of this metal in such combinations.

Practically any analysis involving these three metals can be readily handled so that a solution adaptable to the above procedure is obtained; in fact, it is generally easier than not so to handle it. Of other metals, tungsten, molybdenum and vanadium can be reduced by the treatment, but are easily removed in the preparation of the solution.

An exception to this generalization should perhaps be made in the case

[1] *Metallurgie*, 7, 711.
[2] Newton, *Am. J. Sci.*, [4] 23, 365.

of certain complex alloy steels, the application to which of the procedure described, while not discouraged, has not as yet been considered in detail.

Summary.

An oxidimetric determination of Ti and Cr, involving the use of an electrically heated reductor, is described, by means of which these metals may be determined easily and accurately, either alone or together with iron and other metals.

The writer wishes to express his appreciation of the services of A. Ortiz and also of H. B. C. Allison, who performed the test analyses cited and suggested the extension of the procedure to Cr.

RESEARCH LAB. GEN. ELECTRIC CO ,
SCHENECTADY, N Y

THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.

BY O. L. BARNEBEY.
Received March 25, 1914

Since the original proposal of the permanganate titration of iron by Marguerite,[1] the method has undergone various modifications. The majority of these changes were made to obviate the high results obtained by titrating in the presence of hydrochloric acid. This error was first pointed out by Löwenthal and Lenssen[2] and later by a number of authors.[3-26] Kessler[4] first called attention to the fact that considerable sulfuric acid, and still better manganese salts, greatly reduced the influence of the hydrochloric acid. Zimmerman[5] then proposed the use of manganese salts for this purpose, claiming as great an accuracy in hydrochloric as in sulfuric acid solutions. Reinhardt[7] next suggested the use of phosphoric acid also, for the removal of the color of ferric chloride to insure a better end point.

The permanganate method, used very largely to-day for the determination of iron in ores, in brief is as follows: Solution of the ore by heating with stannous chloride and hydrochloric acid, completion of the reduction by adding stannous chloride to the hot solution until colorless, diluting, addition of mercuric chloride to remove the excess of stannous salt, addition of the Zimmerman-Reinhardt solution (sometimes known as "preventive solution") containing sulfuric acid, manganese sulfate and phosphoric acid, and titration with permanganate, taking the first recognizable tint of color, permeating the entire solution for a short time, as the end point (inasmuch as the end point is somewhat unstable in the presence of chlorides).

The question which has concerned most of the authors quoted is: Does the Zimmerman-Reinhardt, or similar solution really prevent the action of hydrochloric acid? Birch[28] maintains that the method is only

an approximate one. However, the concensus of opinion of the various workers is that, if used in sufficient quantity, it stops practically all, if not all, of the influence of small amounts of hydrochloric acid. Friend[24] says the concentration of hydrochloric acid should not be greater than 0.25 M. Jones and Jeffreys[22] find a constant error, which is not obviated by any concentration of hydrochloric acid or manganese sulfate mixture. They recommend a subtraction of this error in each determination. To test this point, a standard solution of ferrous sulfate, containing sulfuric acid, was prepared and its strength determined by permanganate titration in sulfuric acid solution. Equal volumes of this solution were then employed for titration with varied quantities of hydrochloric acid and preventive solution.

General Reagents.

The Reinhardt-Zimmerman solution was made as follows: 160 g. of crystallized manganese sulfate, 330 cc. phosphoric acid (sp. gr. 1.7) and 320 cc. of sulfuric aicd (sp. gr. 1.84) diluted to 2400 cc. It is also designated manganese solution No. 1, to distinguish it clearly from other preventives employed. This solution is in general use for the titration of iron.

Other reagents used in this and other series are as follows. Hydrochloric acid, sp. gr. 1.10; sulfuric acid, sp. gr. 1.40; phosphoric acid, sp. gr. 1.35; mercuric chloride, a saturated solution; stannous chloride, 200 g. $SnCl_2.2H_2O$ and 70 cc. HCl (sp. gr. 1.20) per liter.

The ferric chloride solutions used in each series following series six were analyzed by the use of the Zimmerman-Reinhardt solution called in this paper "manganese solution No. 1." At least one result is given in each series. Where only one result is given it is an average of two or more analyses.

Special reagents for individual series will be described in connection with the series in which they are used.

Volume of Solutions Titrated.

Unless otherwise stated, the volume of the solution after dilution just preceding titration was about 500 cc. In most cases a considerable deviation from this volume is of very little consequence, but for the general purposes of this paper it is important.

Use of Preventives Containing Manganese.

Table I shows very concretely that no correction for an inherent error of the Zimmerman-Reinhardt method is necessary. However, it is easy to conceive a trace of iron in a reagent such as the stannous chloride, which, if used for the reduction of all the iron present, would introduce a fairly uniform error of the nature described by Jones and Jeffreys.[22]

A number of authors recommend a time interval between the addition of the mercuric chloride and manganese sulfate solution. In some cases

TABLE I.

Series I.—Accuracy of the Zimmerman-Reinhardt Method.

20 cc. of $FeSO_4$ solution = 0.1338 g. Fe.   1 cc. of $KMnO_4$ solution = 0.004386 g. Fe.[1]

Expt. No.	Wt. Fe taken.	Cc. HCl.	Cc. H_2SO_4.	Cc. manganese soln. No. 1.	Cc. $SnCl_2$.	Cc. $HgCl_2$.	Wt. Fe found.	Deviation from H_2SO_4 result.
1	0.1338	..	20	..	....	..	0.1338	....
2	0.1338	..	20	..	....	..	0.1338	....
3	0.1338	..	20	20	....	..	0.1337	—0.0001
4	0.1338	5	.	20	....	..	0.1338	±0.0000
5	0.1338	10	..	20	....	..	0.1337	—0.0001
6	0.1338	10	.	20	. ..	..	0 1337	—0.0001
7	0.1338	25	.	20	....	..	0 1339	+0.0001
8	0.1338	40	..	20	....	..	0.1351	+0.0013
9	0.1338	5	..	..	....	..	0 1368	+0.0030
10	0.1338	10	.	20	0.06	10	0.1338	±0.0000
11	0.1338	10	..	20	0.10	10	0.1337	—0 0001
12	0.1338	10	..	20	0.20	10	0.1338	±0.0000

even ten minutes[26] is designated. This was investigated by titrating: (1) with a time interval of twenty seconds, (2) of thirty seconds, (3) of ten minutes, using the solutions employed in Table I. In (1) and (2) vigorous stirring with a rather heavy glass rod accompanied the addition of the tin salt and continued until the end of the titration

TABLE II.

Series II.—Interval of Time Necessary Just before Titration. 1 cc. $KMnO_4$ = 0.004386 g. Fe. 20 cc. $FeSO_4$ (= 0.13 g. Fe) + 10 cc. HCl + 10 cc. $HgCl_2$ + 20 cc. Mn sol. No. 1 taken.

No.	Cc. $SnCl_2$.	Time interval.	Wt. of Fe found.
1	0.06	20 sec.	0.1338
2	0.10	20 sec.	0.1340
3	0.10	30 sec.	0.1338
4	0.10	30 sec.	0.1338
5	0.10	10 min.	0.1330
6	0.10	10 min.	0.1340

Series III.—Effect of Speed of Titration. 1 cc. $KMnO_4$ = 0.004836 g. Fe. 20 cc. $FeCl_3$[2] (= 0.1717 g. Fe)   10 cc. HCl taken.

Cc. Mn soln. No. 1.	Time. Min.	Sec.	Wt. Fe found. G.
20	2	30	0.1717
20		45	0.1718
5	2	30	0.1717
5		45	0.1732
3	2		0.1719
3		45	0 1739
2	2	30	0.1729
2	1	45	0.1727
2	1	10	0 1732
2		45	0.1739
2		10	0.1755

These results show that only a short interval of time is necessary be-tween the addition of stannous chloride and mercuric chloride, if the solution is thoroughly agitated.

[1] This is the average value obtained by checking the solution against electrolytic iron, sodium oxalate and ferrous ammonium sulfate. All the permanganate solutions used in this investigation were standardized in a similar manner.

[2] This solution contained 10 cc. HCl (1.2) per liter.

Speed of Titration.

Many series of analyses have been made in which the influence of the speed of titration was closely watched. In this study the permanganate was added at as nearly a uniform rate as possible until the end point was closely approached and then the titration was finished more slowly. The solutions were stirred vigorously during the entire titration to give uniformity of mixing. Series III is typical of the results obtained.

Another of the several series of analyses was performed using ferrous sulfate as the standard iron solution with analogous results.

The results of Series III seem to justify the conclusion that, if the action of the hydrochloric acid has been offset by a sufficient excess of the preventive, no difference enters except the difference in buret drainage. (See also Series I.) However, if the amount of preventive just sufficient for a good result with considerable hydrochloric acid present in a slow titration be used under the same conditions, except in a faster titration, then more permanganate is required. This confirms the work of Friend.[24]

In the work outlined in the following pages the solutions were stirred thoroughly and the buret allowed to give a uniform flow of permanganate until the end point was nearly approached, then the titration was finished more slowly, as indicated above. About 1 cc. for each 2 seconds was the rate adopted as a convenient basis for comparison of results.

Effect of HgCl in Suspension.

In a large number of titrations, in which an amount of preventive insufficient to stop the action of hydrochloric acid on the permanganate was used, a partial or complete disappearance of the calomel was noticed. This suggested the action of chlorine or hypochlorous acid on the mercurous chloride, thus reducing the concentration of active oxidizing agent in solution and correspondingly lowering the speed of oxidation of ferrous iron, hence requiring more permanganate to complete the reaction. To test this, measured portions of standard ferric chloride solution were acidified with 10 cc. of hydrochloric acid (sp. gr. 1.10), heated, reduced with stannous chloride as usual, and diluted; mercuric chloride was added and the calomel filtered out. To the filtrates were added varying amounts of stannous chloride (40 g. per liter) and the titration was finished as before indicated. No preventive was used in this series. Meineke[11] likewise calls attention to the influence of calomel on the titration.

All the end points were indefinite, becoming more so as the quantity of calomel increased. The first semi-permanent tinge throughout the solution was taken as the end point. These results show that when the hydrochloric acid is allowed to interfere in titration the amount of interference is somewhat proportional to the concentration of calomel in suspension.

TABLE III

Series IV —Effect of Suspended Calomel

Expt. No	Wt of Fe taken	Cc HCl	Cc HgCl	Excess of SnCl₂ Cc	Wt of Fe found
1	0 1930	10	20	1	0 2039
2	0 1930	10	20	1	0 2035
3	0 1930	10	20	2	0 2075
4	0 1930	10	20	3	0 2101
5	0 1930	10	20	3	0 2105
6	0 1930	10	20	5	0 2149

Quantity of Manganese Solution Required.

A series of analyses was made by reducing measured portions of a ferric chloride solution, adding the other reagents as in Series III, but using varying quantities of the manganous sulfate solution mixture   Another series was made keeping the manganous sulfate solution constant   In each determination one drop of stannous chloride was added in excess and the resulting calomel left in suspension

TABLE IV

Series V —Quantity of Manganese Sulfate Soln Required

1 cc of KMnO₄ = 0 004887 g Fe   20 cc of FeCl₃(= 0 2290 g Fe) + 10 cc HgCl₂ taken

Cc HCl	Cc manganese soln No 1	Wt of Fe found	Comment	Cc HCl	Cc manganese soln No 1	Wt of Fe found	Comments
5		0 2346	End point unstable	10	20	0 2292	
5	1	0 2331	End point unstable	15	20	0 2290	
5	2	0 2314	End point unstable	20	20	0 2292	
5	3	0 2302	End point more stable	25	20	0 2290	
5	4	0 2299	End point more stable	30	20	0 2292	
5	5	0 2299	End point more stable	35	20	0 2292	
5	6	0 2290	End point good	40	20	2299	Part of HgCl dissolved
5	6	0 2287	End point good	50	20	2316	Part of HgCl dissolved
5	10	0 2287	End point good	55	20	2316	Part of HgCl dissolved
5	20	0 2290	End point good	60	40	2297	Part of HgCl dissolved
5	20	0 2290		75	40	0 2302	Part of HgCl dissolved
5	20	0 2290		75	40	0 2302	Part of HgCl dissolved
				120	80	0 2321	All of HgCl dissolved

The lower limit of accuracy under the conditions obtaining is seen to be 6 cc. of manganese solution mixture for five cc. of hydrochloric acid added to the other chlorides present.   This amount would probably be somewhat different for varying quantities of ferric chloride and slightly varying with different individuals because of differences in manipulation.

Manganese Solutions with and without Phosphoric Acid.

A manganese sulfate solution containing 160 g. of crystallized salt in 2400 cc. was prepared and used in the following series   (This solution is designated "manganese solution No. 2 ")

TABLE V

Series VI.—Use of H_3PO_4 and H_2SO_4 with $MnSO_4$.

1 cc $KMnO_4$ = 0 004847 g. Fe   20 cc $FeCl_2$ (= 0 2101 g. Fe, Experiments 1–15 inclusive) and 20 cc $FeCl_2$ (= 0 2310 g Fe, Experiments 16–28 inclusive) + 10 cc HCl + 10 cc. $HgCl_2$ taken

Expt. No	Cc. manganese soln No 2.	Cc H_2SO_4	Cc. H_3PO_4	Wt of Fe found	Deviation	Expt. No.	Cc manganese soln No 2	Cc H_2SO_4	Cc H_3PO_4	Wt of Fe found	Deviation
1	1			0 2201	+0 0100	16		12		0 2375	+0 0065
2	2			0 2205	+0 0104	17		12		0 2382	+0 0072
3	3			0 2167	+0 0066	18			12	0 2363	+0 0053
4	6			0 2133	+0 0032	19			12	0 2375	+0 0074
5	10			0 2133	+0 0032	20	25			0 2322	+0 0012
6	15			0 2128	+0 0027	21	25		10	0 2307	—0 0003
7	25			0 2118	+0 0017	22	25		10	0 2307	—0 0003
8	50			0 2101	+0 0000	23	25			0 2322	+0 0012
9	50			0 2104	+0 0003	24	25		5	0 2310	+0 0000
10	25	12		0 2101	+0 0000	25	25	5		0 2312	+0 0002
11	15	8		0 2104	+0 0003	26	25	5		0 2312	+0 0002
12	10	5		0 2133	+0 0032	27	25	5		0 2310	+0 0000
13	10	15		0 2121	+0 0020	28	25		5	0 2310	+0 0000
14	10	30		0 2106	+0 0005						
15	10	50	.	0 2123	+0 0022						

This series shows (1) that manganese sulfate without sulfuric or phosphoric acid will prevent the effect of hydrochloric acid on the permanganate, (2) that a less amount of manganese sulfate is required when it is accompanied by sulfuric or phosphoric acids, and (3) that sulfuric and phosphoric acids can be used interchangeably.

On account of the fact shown in Series V, that the phosphoric and sulfuric acids could be used interchangeably, it seemed worth while to make a solution of manganese sulfate in sulfuric acid and test its prevention. Consequently a solution was prepared containing 70 g. of crystallized salt and 300 cc. of sulfuric acid (sp. gr. 1.84) per liter. (This solution is designated "manganese solution No. 3.")

These results show that the use of phosphoric acid is merely a matter of preference. Except in the cases where 40 cc. of hydrochloric acid was present, one solution seemed to be as good as another; however, in the latter case, what difference does exist is in favor of the phosphoric acid. Of course, no such volumes of hydrochloric acid are used in the analysis of iron ores, making this point of less consequence.

A series of analyses was made using manganese chloride solution as preventive, thus eliminating sulfates and phosphates entirely. While the end points were obscure on account of color of the solution, nevertheless comparatively good results were obtained, showing good prevention. In this series (VIII) the following solutions were used: A ferrous chloride solution máde by dissolving approximately 25 g. of the crystallized salt

TABLE VI

Series VII.—Titration without H_3PO_4

1 cc. $KMnO_4$ = 0.004396 Fe. 20 cc $FeCl_2$ (= 0 2092 g Fe) + 10 cc $HgCl_2$ taken.

Expt. No.	Cc. HCl.	Cc. manganese soln. No. 3.	Wt. of Fe found.	Comments
1	5	1	0 2123	
2	5	2	0 2112	
3	5	3	0 2105	
4	5	4	0 2098	
5	5	5	0 2101	(Rather heavy HgCl)
6	5	6	0 2098	
7	5	6	0 2096	
8	5	6	0 2096	
9	5	7	0 2092	
10	5	8	0 2092	
11	10	5	0 2105	
12	10	10	0 2092	(Light HgCl)
13	10	10	0 2101	(Rather heavy HgCl)
14	10	15	0 2092	
15	10	15 cc manganese soln No 1	0 2092	
16	10	25	0 2090	
17	20	20	0 2090	
18	20	20	0 2092	
19	20	20 cc manganese soln No 1	0 2092	
20	40		0 2180	
21	40	20	0 2096	Very slow titration
22	40	20 cc manganese soln No 1	0 2096	Very slow titration

in a liter of water containing 10 cc. of hydrochloric acid (sp. gr. 1.2); a manganese chloride solution containing 75 g. of crystallized salt and 20 cc. of hydrochloric acid (sp. gr. 1.2) per liter; hydrochloric acid, sp gr. 1.1. All the titrations were performed somewhat slower than usual, about two minutes being required for each titration.

TABLE VII.

Series VIII.—Manganese Chloride as Preventive

1 cc. $KMnO_4$ = 0 004836 g Fe 20 cc $FeCl_2$ (= 0.1717 g. Fe) + 5 cc HCl taken

Cc. MnCl₂.	Cc manganese soln No 1	Wt. of Fe found.	Cc MnCl₂	Cc. manganese soln. No 1	Wt. of Fe found
.	20	0.1717	10		0 1722
.	20	0.1717	12		0 1722
..	..	0.1755	16		0.1724
1	..	0 1745	20		0 1722
2	..	0.1743	25		0 1722
3	.	0.1740	50		0 1719
4	.	0.1740	50	.	0.1719
5	..	0.1732	50		0.1722
6	..	0.1734	100		0 1722
7	..	0.1729	100		0.1719
8	..	0.1732	200	..	0.1719

Application of Other "Preventives."

The role which manganese salts play in preventing the action of hydrochloric acid on the permanganate in titration seemed to warrant a study of other substances to ascertain their action toward prevention.

The first class of substances tried were neutral salts. Skrabal[16] has studied the influence of the addition of varying amounts of normal neutral salt solutions in the titration of iron, arriving at the conclusion that these salts do not produce correct results. In this work much stronger solutions are employed, which accounts for somewhat different results. Sodium silicate, borate and tetraborate give some prevention, but the adjustment between the amount of salt and acid to be used was too difficult to give any merit to the procedure. If too much silicate is used the ferrous iron precipitates and if too much sulfuric acid is added the end point is indistinct, overtitration resulting. Sodium sulfate, when used in large enough amounts, gives a good titration. Potassium sulfate is not as effective, probably because of its limited solubility in water. Ammonium sulfate also prevents moderately well with low concentrations of hydrochloric acid and high concentrations of the ammonium salt, but is not as satisfactory as the former two. These observances are in contradiction to the work of Birch,[21] who says that sodium sulfate and magnesium sulfate do not prevent, and that ammonium sulfate is worse than worthless.

TABLE VIII

Series IX —Na_2SO_4 10 H_2O (250 g in Liter) as Preventive 1 cc $KMnO_4$ = 0 004887 g Fe   20 cc $FeCl_2$ (= 0 1930 g Fe) + 10 cc $HgCl_2$ taken

Series X —K_2SO_4 as Preventive 1 cc $KMnO_4$ = 0 004887 g Fe   20 cc $FeCl_2$ (= 0 2290 g Fe) + 10 cc $HgCl_2$ taken.

Expt No	Cc HCl	Cc Na_2SO_4	Wt of Fe found	Expt No	Cc HCl	Cc $HgCl_2$	Cc K_2SO_4	Wt. of Fe found
1	25	100	0 1961	1	5	10	50	0 2297
2	25	200	0 1961	2	5	10	50	0 2297
3	25	200	0 1056	3	10	10	50	0 2312
4	25	300	0 1937	4	15	10	50	0 2331
5	25	400	0 1930	5	10	10	100	0 2299
6	25	400	0 1930	6	15	10	100	0 2301
7	25	400	0 1930	7	20	10	100	0 2326
8	5	20 cc Mn soln No 1	0 1930	8	25	10	200	0,2306
				9	25	10	200	0 2304
				10	5	10	20 cc Mn soln No 1	0 2290

Another series of results was obtained preceding this series, in which was used a supersaturated solution of sodium sulfate of about twice the strength of the one here employed. A correspondingly less volume of the sulfate solution was necessary for prevention.

In Series X are tabulated the results obtained using a saturated solution of potassium sulfate and from these results it is evident that potassium

ate solutions do not contain sufficient alkali sulfate for good pre
ventive purposes.

Cady and Ruediger[9] have published a method using mercuric sulfate as
reagent to stop the influence of hydrochloric acid.   To study the action
of this reagent, 300 g. of mercuric sulfate was dissolved in 1400 cc. of water
containing 125 cc. of sulfuric acid (sp. gr. 1 84) and the solution applied
in Series XI.

TABLE IX

Series XI — Mercuric Sulfate as Preventive

1 cc KMnO₄ = 0 004887 g Fe   20 cc FeCl₃ (= 0 2150 g Fe) + 5 cc HCl taken

Expt. No	Cc. HgCl₂	Cc HgSO₄	Cc manganese soln No 1	Wt of Fe found	
1	10	10		0 2118	
2		10		0 2167	Indefinite
3		15	.	0 2155	
4	10	20		0 2167	Indefinite
5	10	25		0 2150	
6		25		0 2150	
7		25		0 2155	
8		35		0 2228	Very indefinite
9	10	50		0 2297	Very indefinite
10	10	50		0 2297	Very indefinite
11	10		20	0 2150	

Results 1 to 4, inclusive, show incomplete prevention due to an insuffi-
cient quantity of mercuric sulfate.   Experiments 5 and 6 were satisfactory.
The results obtained in Experiments 8 to 10, inclusive, were decidedly high,

TABLE X

Series XII —Potassium and Sodium Acid Sulfates as Preventives

1 cc KMnO₄ = 0 004887 g Fe   20 cc FeCl₃ (= 0 1596 g Fe) + 10 cc HgCl₂ taken

KHSO₄ = saturated solution

Expt No.	Cc HCL	Cc H₂SO₄	Cc KHSO₄	Wt of Fe found		Expt No	Cc HCl	Cc H₂SO₄	Cc KHSO₄	Wt of Fe found	
1	5			0 1671	HgCl disappeared	15	20		150	0 1618	
2	5	25		0 1618		16	20		175	0 1628	
3	5		25	0 1603		17	20		200	0 1637	
4	5		25	0 1603		18	20		500	0 1630	
5	5		50	0 1598		19	5		100	0 1596	
6	5		50	0 1596		20	5		100	0 1598	
7	5	25	50	0 1613				NaHSO₄ = 500 g per liter			
8	5	50	50	0 1637		1	5		25	0 1598	
9	10		25	0 1681	HgCl disappeared	2	10		25	0 1613	
10	10		50	0 1600		3	10		50	0 1603	
11	15		50	0 1623		4	15		50	0 1625	
12	15		75	0.1600		5	15		75	0 1620	
13	20		100	0 1613		6	15		100	0 1623	
14	20		125	0 1618		7	5		20 cc Mn soln No. 1	0.1596	

due apparently to the transposition of mercurous chloride to mercurous sulfate by the mercuric sulfate. This point is mentioned in Cady and Ruediger's[2] original paper. The difficulty of adjustment of the quantity of mercuric sulfate to the other variables of an iron determination reduces the value of such a reagent as mercuric sulfate.

Sodium acid sulfate and potassium acid sulfate prevent quite well when the quantity of hydrochloric acid to be counteracted is small. With larger amounts of hydrochloric acid or in the presence of sulfuric acid with the smaller quantities of hydrochloric acid, results are not as good.

Experiments 5 and 6 indicate that about 50 cc. of 50% potassium acid sulfate solution is necessary to stop the detrimental influence of 5 cc. of hydrochloric acid. Experiments 7 and 8 show higher titration results with sulfuric acid than without it. Numbers 19 and 20 indicate that an excess of the potassium acid sulfate does not give a higher value if the

<div align="center">TABLE XI.</div>

<div align="center">Series XIII.—Magnesium and Zinc Sulfates as Preventives.</div>

1 cc. $KMnO_4$ = 0.004847 g. Fe. 20 cc. $FeCl_3$ (= 0.2283 g. Fe) + 10 cc $HgCl_2$ taken.
$MgSO_4$ solution = $MgSO_4.7H_2O$ — 500 g. per liter.

Expt. No.	Cc. HCl.	Cc. MgSO₄	G. Fe found.	
1	5	..	0.2283	20 cc. Mn soln. No. 1 added
2	5	50	0.2283	
3	5	50	0.2285	
4	10	50	0.2293	HgCl partially disappears
5	10	100	0.2297	
6	10	150	0.2293	HgCl partially disappears
7	10	200	0.2293	HgCl partially disappears
8	15	50	0.2297	HgCl partially disappears
9	20	50	0.2327	HgCl partially disappears
10	25	50	0.2346	HgCl partially disappears
11	10	..	0.2366	HgCl disappears entirely

1 cc. $KMnO_4$ = 0.005309 g. Fe. 20 cc. $FeCl_3$ (= 0.2283 g. Fe) + 10 cc. $HgCl_2$ taken.
$ZnSO_4$ soln. = 500 g. $ZnSO_4.7H_2O$ per liter.

1	5	..	0.2283	20 cc. Mn soln. No. 1 added
2	5	..	0.2378	
3	5	20	0.2296	
4	5	25	0.2293	
5	5	50	0.2293	
6	5	100	0.2293	
7	5	200	0.2291	
8	25	100	0.2325	*HgCl disappears*
9	25	200	0.2304	*HgCl partially disappears*
10	10	50	0.2293	
11	15	50	0.2309	
12	15	100	0.2393	
13	20	125	0.2309	
14	20	200	0.2309	
15	20	250	0.2291	

amount of hydrochloric acid remains the same. However, in numbers 13 to 18 inclusive, in which the amount of acid was 20 cc., the potassium bisulfate gave a progressively higher titration as its concentration was increased. Sodium acid sulfate showed somewhat the same kind of deportment. These acid sulfates while possessing preventive powers do not have this quality to a sufficient degree to make them suitable for an accurate titration of iron.

Magnesium sulfate and zinc sulfate produce decided effects in checking the influence of hydrochloric acid, the former being more efficient than the latter.

Scrutiny of Table XI shows good results in only two cases when magnesium sulfate was used, e. g., Experiments 2 and 3, in which only 5 cc. of hydrochloric acid was added. In the zinc sulfate series all the results were too high. Almost identical volumes of permanganate were required for 5 cc. of hydrochloric acid within a range of 25 to 200 cc. of the zinc sulfate solution. A somewhat analogous set of figures was obtained for 10 cc. of hydrochloric acid within a range of 50 to 200 cc. of the magnesium sulfate. These results show a tendency toward prevention, which, nevertheless is not sufficient for practical application in titrating iron

Chromium and ferric sulfates were found to have no value as preventives of the high results due to the action of hydrochloric acid on permanganate. High concentrations of chromium were naturally impossible on account of the color imparted to the solution.

TABLE XII.

Series XIV —Potassium Phosphate Mixtures as Preventives.

K_3PO_4 solution = 500 g K_3PO_4 per liter

20 cc $FeCl_3$ = 0 2031 g Fe + 10 cc $HgCl_2$ taken

1 cc $KMnO_4$ = 0 004887 g Fe

Expt. No	Cc HCl	Cc. H_3PO_4	Cc K_3PO_4	Cc H_2SO_4	Wt. of Fe found	Expt No	Cc HCl	Cc H_3PO_4	Cc K_3PO_4	Cc H_2SO_4	Wt of Fe found
1	5	.			0 2031[1]	13	5	30	10		0 2033
2	5	..			0 2028[1]	14	5	30	10		0 1891[2]
3	5	.			0 2031	15	10	30	10		0 2031
4	5	.			0 2055	16	5	30	20		0 2004
5	10				0 2160[3]	17	25	30	10		0 2072
6	25				0 2189[3]	18	25	50	20		· 0 2051
7	50				0 2180[3]	19	25	50	30	.	0 2009
8	5	.	10	30	0 1906[3]	20	25	75	30		0 2026
9	5	.	10	30	0 2048	21	25	100	30		0 2031
10	5	.	10	30	0 1899[3]	22	25	200	30		0 2031
11	5	..	10	30	0 2053	23	25	200			0.2063
12	5	30	10		0 2031	24	5				0.2031
						25	5				0 2033

[1] 30 cc. manganese soln. No. 1 added

[2] HgCl dissolved almost completely

[3] Added K_3PO_4 before the acid (H_3PO_4 or H_2SO_4) + 50 cc manganese soln No 1 added.

Mixtures of tri-potassium or disodium phosphate and phosphoric acid were found to produce excellent prevention.

Experiments 1, 2, 3, 24, 25 are titrations with "manganese sulfate solution No. 1." Experiments 8, 10, 14, show the influence of adding the alkaline phosphate before the acid. In all likelihood some of the iron is precipitated as ferrous phosphate in these cases, yielding low results. Experiments 16, 19, 20, indicate an insufficiency of acid to keep the ferrous phosphate from forming. Experiments 12, 13, 15, 21, 22, show that when the proper adjustment of phosphoric acid and potassium phosphate is obtained correct results follow. A proportion of not less than three volumes of 1–1 phosphoric acid to 1 volume of 50% K_3PO_4 gives the best results. A solution containing 500 g. of tripotassium phosphate (or its equivalent in dipotassium phosphate) and 1500 cc. of phosphoric acid (sp. gr. 1.7) diluted to two liters can be used instead of the separate reagents. Twenty cc. of this solution will stop the action of 5 cc. and 60 cc. suffice for 25 cc. of hydrochloric acid (sp. gr. 1.10).

Series XIII a saturated solution of $Na_2HPO_4.12H_2O$ was employed.

TABLE XIII.

Series XV   Disodium Phosphate Mixtures as Preventives

10 cc $FeCl_3$ = 0.2280 g Fe + 10 cc $HgCl_2$ taken

1 cc $KMnO_4$ = 0.004887 g Fe

Expt. No	Cc HCl	Cc Na2HPO4	Cc H3PO4	Wt of Fe found	Expt No	Cc HCl	Cc Na2HPO4	Cc H3PO4	Wt of Fe found
1	5	50	100	0.2280	8	50	50	100	0
2	10	50	100	0.2280	9	60	50	100	0
3	15	50	100	0.2284	10	100	50	100	0.921[1]
4	20	50	100	0.2282	11	5	5	10	0.287
5	25	50	100	0.2280	12	5	10	20	.2280
6	30	50	100	0.2280	13	5	20	40	0.2278
7	35	50	100	0.2282	14	5	20 cc manganese soln No. 1		0.2280

This series shows excellent prevention, even 35 cc. of hydrochloric acid being taken care of nicely, and 50–100 cc. did not produce an error such as one might anticipate.

The phosphoric acid and sodium phosphate may be combined into one solution by preparing as follows: Solution of 500 g. of disodium phosphate in 1000 cc. of phosphoric acid and 500 cc. of water then dilution to 2000 cc. Thirty cc. is a sufficient quantity for 10 cc. and 100 cc. are enough to offset the action of 25 cc. of hydrochloric acid.

Cerium sulfate gives excellent prevention of the hydrochloric acid interference. In fact it works as effectively as manganous sulfate when its efficiency is measured on the basis of gram equivalents. 20 g. of $Ce_2(SO_4)_3.8H_2O$ were dissolved in 250 cc. of water to be used in the following series:

[1] End point unstable

TABLE XIV

Series XVI.—Cerium Sulfate as Preventive. 20 cc. FeCl$_2$ (= 0.2291 g. FeCl$_2$) + 10 cc. HgCl$_2$ taken. 1 cc. KMnO$_4$ = 0.004887 g. Fe.				Series XVII.—Cerium Sulfate Mixture[1] as Preventive. 20 cc. FeCl$_2$ (= 0.1571 g. Fe) + 10 cc. HgCl$_2$ taken 1 cc. KMnO$_4$ = 0.004887 g. Fe			
Expt. No.	Cc. HCl.	Ce$_2$(SO$_4$)$_2$ soln. Cc	Wt of Fe found	Expt. No.	Cc HCl	Ce$_2$(SO$_4$)$_2$ soln. Cc	Wt of Fe found.	Comments.
1	5	10	0 2309	1	5	5	0 1583	
2	5	20	0 2291	2	5	10	0 1570	Slow titration
3	5	20	0 2293	3	5	10	0 1579	Rapid titration
4	5	20	0 2293	4	5	15	0 1572	Rapid titration
5	10	20	0 2299	5	5	25	0 1572	Rapid titration
6	7	20	0 2293	6	10	20	0 1574	Slow titration
7	5	25	0 2293	7	20	20	0 1614	Rapid titration
8	5	35	0 2288	8	20	35	0 1572	
				9	5	20 cc Mn	0 1571	
9	5	50	0 2288			soln. No. 1		
10	5	20 cc. Mn soln. No 1	0 2291					

Thus it is to be seen that Ce$_2$(SO$_4$)$_3$ is very effective in stopping the detrimental nature of hydrochloric acid on permanganate, its value being commensurate with MnSO$_4$.

Theoretical.

A number of explanations have been offered to explain the function of manganese salts in the iron titration with permanganate. Volhard[35] explains the action by assuming the formation of tetravalent manganese (MnO$_2$) which then oxidizes the ferrous iron more rapidly than it does hydrochloric acid. Wagner[49] assumes the intermediate formation of FeCl$_2$.2HCl in the absence of manganese sulfate, which oxidizes very rapidly, consuming more permanganate than is required for ferrous iron. Zimmerman[5] suggested that, in absence of manganese salts, the iron is converted into a peroxide which is unstable and at once forms ferric iron and oxygen, the latter acting upon the hydrochloric acid. Manchot[60] explains the action by assuming the formation of "primary oxides" of the peroxide nature, but which tend to revert immediately to oxides of a lower state of oxidation. According to this theory oxidation caused by oxygen forms FeO$_2$; by permanganate, chromic acid, hydrogen peroxide, etc., Fe$_2$O$_5$; and with hypochlorous acid, FeO$_3$. Hence the reaction is assumed to go somewhat as follows: Oxygen forms FeO$_2$, FeO$_2$ oxidizes FeO to Fe$_2$O$_3$, Mn$_2$O$_7$ oxidizes FeO to Fe$_2$O$_5$ with the formation of MnO$_2$, the MnO$_2$ then oxidizes FeO to Fe$_2$O$_3$. If the hydrochloric acid is too

[1] A solution of mixed earth sulfates when analyzed was found to contain 65 g Ce$_2$(SO$_4$)$_3$.8H$_2$O + 200 cc. H$_2$SO$_4$ per liter. This solution was used as was the cerium sulfate of the preceding series.

strong then the Fe_3O_4 reacts with the HCl, liberating chlorine. Birch[33] suggests the formation of $MnCl_4$, which in turn has a greater tendency to oxidize ferrous iron than hydrochloric acid. This last assumption seems to warrant a more general consideration than has been accorded to it. While hydrated manganese peroxide can be assumed to exist for a brief space of time in the hydrosol condition, yet $MnCl_4$ has not been definitely proven to exist in such a solution. The same argument can be applied to a theory requiring assumptions of FeO_2, FeO_3, Fe_2O_5.

Pickering[36] has shown that when manganese dioxide is treated with hydrochloric acid manganese sesquichloride results. A number of other authors have studied the formation of trivalent manganese in solution, especially sulfuric, hydrochloric, hydrofluoric, and phosphoric acids and alkaline cyanides, a number of trivalent salts and double salts being separated from such solutions. (See references under heading, "Theoretical.") Meyer[50] has recently pointed out the definiteness of these compounds in acid solutions and also shows that even when potassium manganicyanide hydrolyzes a trivalent manganihydroxide results. Schilow[51] has explained the reaction of potassium permanganate with oxalic acid on the basis of the intermediate formation of trivalent manganese. Skrabal[16] outlines the oxalic acid oxidation and also that of manganese in alkaline solution through the formation of manganese of the valence of three. Muller and Koppe[44] point out an error in the titration of manganese by the permanganate method in the presence of fluorides due to the formation of MnF_3 and $2KF.MnF_3$.

When potassium permanganate is added to a manganese solution containing an excess of phosphoric acid a deep red to violet coloration is obtained; when added to a manganese solution with hydrochloric acid in excess a greenish brown to black solution results; when added to a manganese sulfate solution in the presence of an excess of sulfuric acid a deep red to purple color is imparted to the solution. Solutions of this nature contain manganese sesquisalts. The possibility of tetravalent manganese being present at ordinary temperatures in significant quantity is apparently quite remote. While very small amounts may be present, practically all attempts to prepare salts in which manganese has the valence of four from such solutions have been negative—only trivalent salts crystallizing from them. More confirmation seems to be necessary to establish the existence of tetravalent manganese in even small quantity in these acid solutions. However, if tetravalent manganese is present the mechanism of the reaction, to be later described would partially be explained through medium of its formation and the fundamental idea of prevention of the chlorine or hypochlorous acid formation remains the same.

In the presence of hydrochloric acid these manganese sesquisalt solutions have a tendency to preserve the oxidation value of the solution; in other

words, prevent the rapid loss of chlorine or hypochlorous acid. This preservation can be shown in open beakers qualitatively in a striking manner by adding 10 cc. of 0.1N permanganate to 50 cc. of 50% manganese sulfate solution containing 10 cc. of concentrated hydrochloric acid and to 50 cc. of water containing a like volume of the acid. In a moderately short time the second solution loses its chlorine in sufficient quantity to become much lighter in color than the first and in a few hours becomes completely colorless, but the solution containing the manganese maintains its color for weeks. Two such solutions in duplicate were prepared August 15 at 9 A.M. Both gave a decided odor of chlorine. At 9 A.M., the following day, the two solutions containing the manganese were still brownish black, but the two without the manganese were practically colorless. On September 5, the two containing the manganese were light brown and on November 18, the color still persisted and a few cc. of the solution gave an evolution of iodine when potassium iodide was added. Water was added from time to time to replace what was lost by evaporation.

In the titration of iron in hydrochloric acid solution it has been shown that manganous and cerous salts used in moderate amounts, and certain acid phosphate and sodium sulfate solutions, prevent the loss of chlorine or hypochlorous acid during titration and enable correct results to be obtained in the presence of hydrochloric acid. Evidently the reactions of these preventives involve two different types of effects. One effect is transposition from chloride to salts of another acid by the mass action of the preventive. The other effect is the formation of an intermediate compound or compounds which have the capacity to oxidize the ferrous iron, preventing the loss of chlorine. In a preventive one of the other effect may be in predominance. In the case of sodium sulfate the first effect is the larger, but some manganese is in solution due to the products of reaction and must exert some influence. In the case of manganese sulfate and sulfuric acid we have both effects with the second the larger, a mixture of sesquichloride and sulfate being produced as intermediate products. When manganese sulfate, phosphoric acid and sulfuric acid are employed, the opportunity for a larger number of sesquisalts to be formed is increased correspondingly, with the same effect as that produced by the more simple mixtures. With manganese chloride as preventive, the intermediate sesquimanganese chloride gives the only effect toward prevention. In these cases the reactions may be represented by the following equations:

(1) (In part), $2KMnO_4 + 10FeCl_2 + 16HCl = 2KCl + 2MnCl_2 + 10FeCl_3 + 8H_2O$

(2) (In part), $2KMnO_4 + 8FeCl_2 + 16HCl = 2KCl + Mn_2Cl_4 + 8FeCl_3 + 8H_2O$

(3) $Mn_2Cl_4 \rightleftharpoons 2MnCl_2 + Cl_2$

(4) $Cl_2 + FeCl_2 = FeCl_3$ (slow)

(5) $Mn_2Cl_4 + 2FeCl_2 = 2FeCl_3 + 2MnCl_2$ (more rapid than 4)
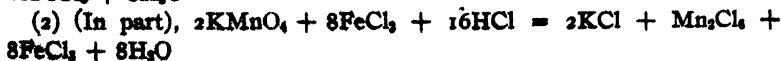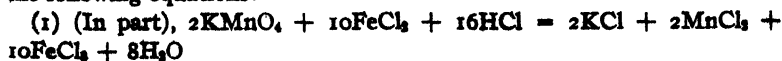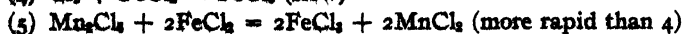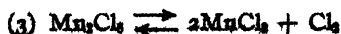
The permanganate oxidizes a considerable portion of the iron according to equation (1). However, some Mn_2Cl_4 is formed, equation (2). This sesquichloride is unstable and has a tendency to decompose, liberating chlorine (3). The smaller the amount of manganese present the more rapid is this decomposition; the larger the amount of manganese the greater the tendency to retard the evolution of chlorine. The chlorine oxidizes the ferrous iron slowly (4). Manganese sesquichloride oxidizes ferrous iron much more rapidly than does free chlorine (5). Hence, if the reaction represented by equation three is forced to proceed toward the left by the addition of manganese chloride, preserving the initial character of the Mn_2Cl_4, the loss of oxidation effect due to chlorine evolution may be prevented and the final reaction follows the theoretical value (1).

When the Reinhardt-Zimmerman, Mixer-DuBois, or other solution of similar nature is employed the first list of reactions takes place partially, but the larger portion of the reaction occurs through the medium of some other acid than hydrochloric—usually phosphoric or sulfuric. In case of sulfuric acid this portion of the reaction can be thus illustrated:

(6) $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$

(7) $2KMnO_4 + 8FeSO_4 + 8H_2SO_4 = K_2SO_4 + 4Fe_2(SO_4)_3 + Mn_2(SO_4)_3 + 8H_2O$

(8) $Mn_2(SO_4)_3 + 2FeSO_4 = 2MnSO_4 + Fe_2(SO_4)_3$
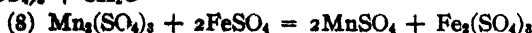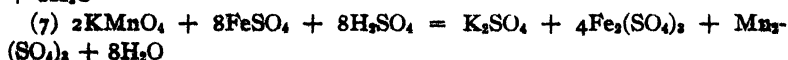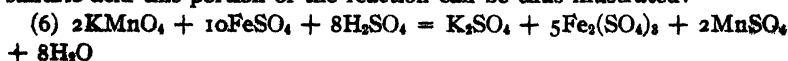
When cerium sulfate is used for the prevention ·

(8a) $\begin{cases} Mn_2(SO_4)_3 + 2Ce_2(SO_4)_3 = 2Ce(SO_4)_2 + 2MnSO_4 \\ 2Ce(SO_4)_2 + 2FeSO_4 = Fe_2(SO_4)_3 + Ce_2(SO_4)_3 \end{cases}$
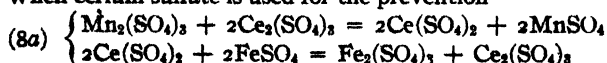
When phosphoric acid is used the reaction probably occurs through the medium of acid phosphates, involving corresponding changes of valence.

Analysis of Iron Ores with Various Preventives.

A number of iron ores were analyzed using the solutions heretofore described: (a) sodium sulfate, (b) potassium phosphate and phosphoric acid, (c) sodium phosphate and phosphoric acid, (d) manganese sulfate and sulfuric acid, (e) manganese sulfate, phosphoric and sulfuric acids, (f) cerium sulfate and sulfuric acid. The sample in each case was decomposed by heating with about 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and sufficient stannous chloride solution to almost reduce all of the iron. After complete solution of the iron, the reduction was finished by adding stannous chloride drop by drop to the hot solution until one drop just made it colorless, then one drop was added in excess. After dilution to about 500 cc., 10 cc. of mercuric chloride was added all at once

with vigorous stirring. One of the preventives above noted was added and the iron titrated. The results from four representative ores are listed below.

TABLE XV

Series XV —Analyses of Iron Ores with Various Preventives

Ore No	Sample No	Wt of sample G	Preventative Kind.	Volume Cc	% Fe found	Ore No	Sample N	Wt of sample G	Preventative Kind	Volume Cc	% Fe found
20	1	0 5000	a	200	65 91	26		0 7000	a	200	35 60
20	1	0 5000	b	30	65 96	26		0 7000	b	30	35 71
20	1	0 5000	c	30	65 96	26		0 7000	c	30	35 64
20	1	0 5000	d	15	65 91	26		0 7000	d	20	35 64
20	2	0 5000	d	15	66 07	26		0 7000	e	20	35 64
20	1	0 5000	e	15	66 07	26		7000	f	30	36 68
20	2	0 5000	e	15	65 96	43		8000	a	200	33 80
20	1	0 5000	f	25	65 96	43		8000	b	25	33 77
20	2	0 5000	f	25	65 98	43	2	8000	b	25	33 54
21	1	0 4000	a	200	57.44	43	3	8000	b	25	33 54
21	1	0 4000	b	25	57 44	43	1	8000	c	30	33 61
21	2	0 4000	b	25	57 50	43	2	8000	c	30	33 86
21	1	0 4000	e	25	57 41	43	1	8000	d	20	33 83
21	1	0 4000	f	30	57 52	43	2	8000	a	20	33 94
						43	1	8000	e	20	33 85
						43	2	8000	c	20	33 79
						43	1	8000	f	20	33 87

Discussion of the End Point.

The end point in the titration of iron is more stable in sulfuric and phosphoric than in hydrochloric acid solutions. In the last named the pink tinge imparted to the solution, showing a slight excess of permanganate, is more fleeting. While the addition of the preventives enumerated allows a correct iron analysis to be made within the range of error expected of such an analysis, nevertheless when the permanganate is added in excess, as at the end of the titration, a fading effect becomes more or less marked. On this account an analyst accustomed to the iron titration in hydrochloric acid solution calls the first slight tinge of color permeating the entire solution the end point. The tinge is much lighter than the tint in sulfuric or phosphoric acid solutions free from hydrochloric acid. This difference is at least partially due to the difference in color of the sesqui chloride and sulfate and phosphate solutions. This variance in stability may account for some of the conflicting analyses heretofore published.

The end point in the titration of ferrous to ferric sulfate in the presence of sulfuric acid and in the absence of hydrochloric acid is almost as clean cut in the ordinary iron analysis as in phosphoric acid solution. Analysts recognize this fact in the standardization of permanganate against ferrous ammonium sulfate and metallic iron, in which case the end point is much more clear than in the regular titration of iron ores in the presence of sus-

pended calomel even when phosphoric acid is added. However, this much must be said, if phosphoric acid is added by an analyst to give what to his eye seems to be a clearer end point in the analysis of the iron containing product, then the analyst who is having trouble with this color change must, to be consistent, add phosphoric acid in standardization if he standardizes the permanganate against an iron containing standard.

One gram of iron present as ferric sulfate with a little free sulfuric acid in a volume of 400–500 cc. gives a recognizable color change with 0.04 cc. of tenth normal permanganate. Of course this coloration is not red or pink, but it is a distinct change of color. Twice the above amount of permanganate gives a very decided coloration. These observations were naturally made against a white background. A moderate amount of experience with the iron titration allows a very sharp end point with moderate amounts of iron (up to about 0.6 g. metal) without the presence of a decolorizing influence, however, when a large amount of iron (over 0.6 g. metal) is to be titrated the addition of phosphoric acid is to be recommended, although, with care, larger amounts can be titrated with accuracy. With smaller amounts the addition of the phosphoric acid is optional with the analyst. Since ordinarily the amount of iron present in the solution being titrated is about 0.3 g. or less it seems to the author that the use of a decolorizer is unnecessary.

Summary.

(1) Correct results are obtained with a mixture of manganese sulfate, sulfuric acid and phosphoric acid for the prevention of the action of hydrochloric acid on permanganate. The use of phosphoric acid in the presence of considerable sulfuric acid in a volume of 400–600 cc. has very little tendency to decolorize the solution, inasmuch as the sulfate solution is practically colorless, except when titrating large amounts of iron. Hence, the elimination or use of phosphoric acid with the sulfuric acid and manganese sulfate is largely a matter of individual preference rather than a fundamental difference in the analysis.

(2) When a titration runs too high, the amount of variance from the true value is dependent on the amount of mercurous chloride present in suspension as well as on the concentration of hydrochloric acid.

(3) Certain neutral sulfates and acid phosphate mixtures react with hydrochloric acid and prevent the latter from causing high results in the iron titration. The acid phosphate solutions are especially serviceable.

(4) Cerous sulfate shows the same deportment in the titrating solution as manganese sulfate.

(5) Sodium sulfate, acid phosphate mixtures, manganese sulfate with sulfuric acid, manganese sulfate with phosphoric acid, or with both acids, can be applied to iron ore analyses. The use of cerous sulfate, while effective, is as yet prohibited on account of the present cost of the chemical.

(6) The prevention of the various reagents studied may be considered of two types: (1) conversion to salts of other acids than hydrochloric by the mass action of the preventor, and (2) the formation of intermediate compounds, which in turn oxidize ferrous to ferric iron with or without the first type being effective at the same time.

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     See also the references under the title "Experimental"

DEPARTMENT OF ANALYTICAL CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON

A NITROGEN GENERATOR.

BY CHAS VAN BRUNT
Received May 4, 1914

A form of generator for producing oxygen-free nitrogen from air, which has some advantages over those hitherto commonly used, has been devised by the writer and has been in constant use for over a year in this laboratory. The absorbing medium for oxygen is the well known copper-ammonium carbonate combination. What novelty there is consists in the continuous circulation of the solution through the copper column in the absorption vessel by means of an air-lift actuated by the incoming air current.

The nitrogen obtained by this means is so far free from oxygen that an incandescent tungsten wire is not oxidized even in a rapid current of the gas. Experience shows this to be a test of great delicacy. As a matter of security, however, it has been usual to add a tube of hot copper to the

system, but there has been so far no experi-
ence to prove that this is necessary, even
for refined work.

The generators in use in this laboratory
have the form and dimensions shown in
the sketch herewith, the size of the reser-
voir A being varied to suit the capacity re-
quired. It is essential that the tube lead-
ing vertically downward from the bottom
of the reservoir shall be long enough to give
a pressure at the level of C, where the air
meets the liquid, such that the volume of
solution carried up may be at least equal to
that of the accompanying air without danger
of the latter backing up into A. The
slight downward slope of the tube C is essen-
tial to the steady operation of the lift. The
internal diameter of the riser tube should
not exceed 5 or 6 mm. unless an unusually
rapid current of gas is required. Adjust-
ment of the relative proportions of air and
solution is made by means of the screw
clamp D. The best results are obtained
when the rate of flow of the solution is such
that it rises as nearly to the top of the
opening into C as is possible without in-
terrupting the down-coming air current at
this point.

The air-liquid mixture is discharged over
the adjustable glass bell in the top of B,
which distributes the liquid over the top of
the column of copper chips or clippings.
Gas and liquid traverse this column to-
gether. The plentiful flow of solution
washes the oxide film from the copper as
fast as it is formed by the action of the in-
coming air, thus maintaining the surface in
active condition. The result is complete
deoxidation of the air, the reaction being
vigorous enough to cause a noticeable rise
in temperature when the current is rapid.
The deoxidized air is delivered as shown,
whence it passes through a purifying train
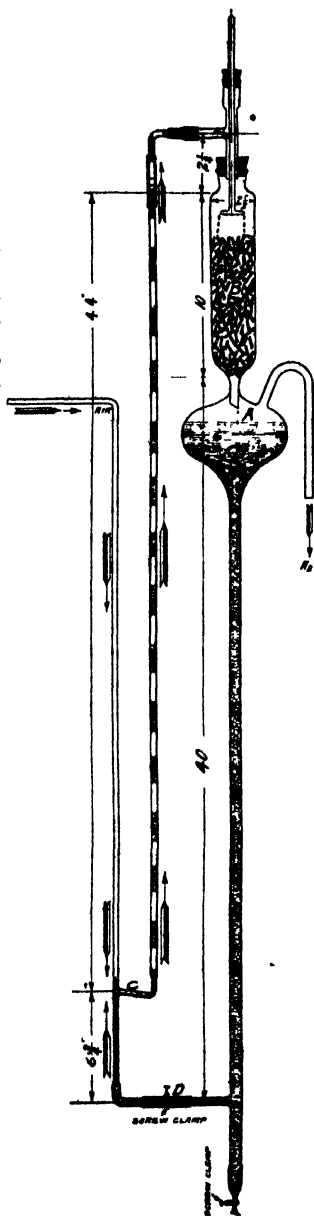
adapted to remove the vapor derived from the solvent. Dilute sulfuric acid is used to remove the ammonia. (The concentrated acid causes stoppage of the tubes, due to separation of solid ammonium sulfate.)

The solution collected in A carries, of course, the copper oxide formed by the wet combustion in B. A good deal of this dissolved copper is reduced to, or remains in, the univalent state in its passage through B, and the reducing energy thus stored is later effectively expended upon the incoming air in the lift.

The solution, as freshly charged to the apparatus, is made by adding to a saturated solution of the "Ammonium Carbonate" of commerce its own volume of ammonia of 0.93 sp. gr. One liter of such a solution may be depended upon for approximately 75 liters of nitrogen from air before becoming exhausted. The approach of this point is accompanied by a dulling of the luster of the copper not difficult to recognize, and also by a slight foaming of the solution. One or two experiments were made which tended to show that equally good results could be obtained by substituting ammonium chloride for the carbonate, maintaining the same molal concentrations of total NH_3 and of the acid radical in each case, namely, about 8 and 2 per liter, respectively, but this has not been tried out in practice.

If the air supply is provided with a safety or reducing valve, the pressure may be left on the apparatus and the nitrogen current started, stopped and regulated by a cock on the delivery tube. The tendency of the air to back out through the reservoir on sudden starting is easily guarded against by a little care; or a check valve may be provided or a downward extension of the tubing if the added vertical extension of the system is not objected to.

In place of air, the oxygen-contaminated nitrogen commonly supplied in pressure tanks has been much used in this laboratory. Of course the life of a charge of solution and copper is greatly extended by this plan.

It may be suggested that the principle of the air-lift as exemplified in the above described device is a laboratory aid which has not had the attention it deserves. That it has other useful applications than the one described is manifest. In designing and adjusting apparatus embodying the principle, it is necessary only to remember that the hydrostatic pressure of the liquid in the reservoir should overbalance that of the column of mixed gas and liquid in the riser by an amount equivalent to the required "velocity head."

RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

NOTE.

Panel for Electro-analysis.—The electrolytic panel, described below, embodies a number of shop kinks which may be of interest to chemists. The

panel itself is of oak, 120 × 60 × 2 cm., and is fastened to the wall by four so called space or shoulder nipples of ($^3/_8$ inch) pipe. These nipples screw into pairs of flanges set on the wall and on the back braces of the panel, respectively.

The centre instrument of the panel has a range of 1 volt, and is used with
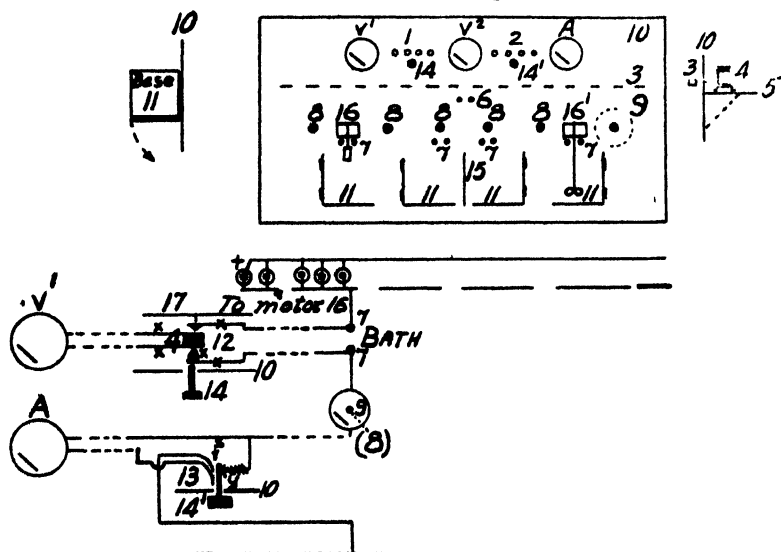
V¹. Bath voltmeter.
A. Bath ammeter.
V². Voltmeter for single potential measurements.
1. Holes for voltmeter connecting plug (14).
2. Holes for ammeter connecting plug (14′).
3. Handles of lamp switches for cutting down 110 volt circuit.
4. Detail of lamp socket and switch (3).
5. Shelf on rear of panel.
6. Binding posts of V².
7. Binding posts for electrodes setting in analysis baths.
8. Twirlers for additional control of baths by means of rheostats (9).
9. Outline of one of six rheostats set on back of panel.
10. Panel board.
11. Beaker support.
12. End view of bank of four switches for voltmeter V¹.
13. End view of bank of four switches for ammeter A.
14, 14′. Plugs for connecting voltmeter and ammeter.
15. Rod for supporting calomel electrode.
16, 16′. Stirring motors with and without clutch.
17. Fiber support for back of voltmeter switch.
x. Brass.
y. Fiber.

the calomel electrode to determine "end points" and single potential differences in the analyses. For convenience the connections of this instrument are brought to the front of the panel, terminating in two binding posts.

The other two instruments have a range of 7.5 volts and 7.5 amperes respectively, and give the current and potential change through the analysis bath. The ammeter is connected through a modified "Jack" switch having four points; and the voltmeter, through a set of four double contact keys. Thus the voltage across and the current through any of the baths may be read by pressing plugs into the proper cavities. There is little sparking ordinarily, as the ammeter connection does not interrupt the current, and the voltmeter set across the bath only.

A double throw switch on the back of the panel allows the use of either 6 volt storage battery or 110 volt lighting current. To reduce the pressure of the latter, three key lamp sockets, wired in multiple, are placed in series with each analysis circuit, and two in each motor circuit. These sockets are set on a shelf attached to the rear of the panel. A neat effect is secured by employing extension keys, the handles of which only are visible on the face of the panel. When the storage battery is used, a fuse plug replaces one of the lamps in each circuit. The meter connections as noted above, are also on the rear of the panel.

Each circuit is further controlled by a nichrome rheostat set in porcelain. These rheostats are screwed to the rear of the panel, and are controlled by cheap typewriter twirlers on the front.

Artificial stirring is accomplished in the outer baths by the use of cheap battery motors with suitable stirrers of glass or platinum clutched (for PbO$_2$) or sealed on to the motor shafts.   HENRY ZIEGEL.

BROOKLINE, MASS

THE COLOR AND IONIZATION OF CRYSTAL-VIOLET.

BY ELLIOT Q. ADAMS AND LUDWIG ROSENSTEIN.

Introduction.

The chromogens[1] derived from triphenylmethane[2] undergo, on the addition of strong acids to their aqueous solutions, a remarkable series of color transformations: The largest variety of color changes among these sub-

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[1] This term will be used to include both colored and colorless modifications.

[2] Kayser, *Handbuch d. Spekt.*, [5] 3, 87, 247, 534; H. W. Vogel, *Ber.*, 11, 622–624 (1878); *Ibid.*, 11, 913–920, 1363–1371 (1878); Berliner, *Ber.*, 1878, 409–431; Girard and Pabst, *Compt. rend.*, 101, 157–160 (1885). J. Formánek. *Unters. u. nachweis organ. Farbstoffe auf spekt. Wege.* (J. Springer, Berlin, 1908).

stances is shown by the dyes, N penta- and N hexa-methyl-p-trianilino-methyl chloride, respectively known as methyl and crystal-violet. Their color, in neutral solution, is blue-violet, changing on the gradual addition of strong acid, through violet-blue, blue, blue-green, green and yellow-green, to a pure yellow in concentrated acid. Accompanying these changes in hue another change takes place when the solutions are allowed to stand, the intensity of the color diminishing greatly in strongly acid or in alkaline solution. In weakly acid solution the fading is slower and less pronounced. Equivalent solutions of all strong acids produce identical effects, and, on neutralization, the original color is in every case restored, in hue at once, and in intensity on standing. Examination with a dark-field ultramicroscope of acidic, neutral and alkaline solutions of crystal-violet showed that only in the last case is this substance colloidal. It is clear from these observations that all these changes are brought about by reactions of the chromogens with hydrogen or hydroxyl ion (or with water), and that all these reactions are completely reversible. Rosaniline, para-rosaniline, malachite green and aniline blue show a series of changes similar in all respects (except that the variation in color is less) to those of methyl and crystal-violet. Solutions of either of the latter are well suited for spectroscopic observations, and at the same time the similarity in behavior and analogy in constitution almost certainly insures identity, in all these cases, of structure and reactions.

The rate of the *development* of color when *alkaline* solutions of triphenylmethane dyes are made acidic with strong or weak acids has been carefully studied by H. C. Biddle;[1] he has pointed out that these changes bear a close resemblance to the slow conversion of the cinchona alkaloids to their toxic isomers, in that the rate of both is greatly decreased by increase in the hydrogen ion concentration. He also called attention to the complexity of the equilibrium in the case of crystal-violet as a result of the possibility of the formation of mono-, di-, and tri-acid salts; and made reference to work bearing on this point already begun at his suggestion by the authors. We wish in this place to express our gratitude to Prof. Biddle for much helpful advice.

The accepted structures for the colorless carbinol (color-base) of crystal-violet and for the violet chloride are shown in the formulas on next page, and if, for convenience, the notation be adopted that the part of compound within the square be represented by R, these formulae become simply, ROH and $\dfrac{Cl}{R}$, whereas the true, (colored) base[2] would be represented by $\dfrac{OH}{R}$. Salt formation at the two remaining nitrogen atoms will be

[1] Biddle, This Journal, 36, 101, 103 (1914).
[2] Cf. Holleman, "Textbook of Organic Chemistry," p. 464 (1903).
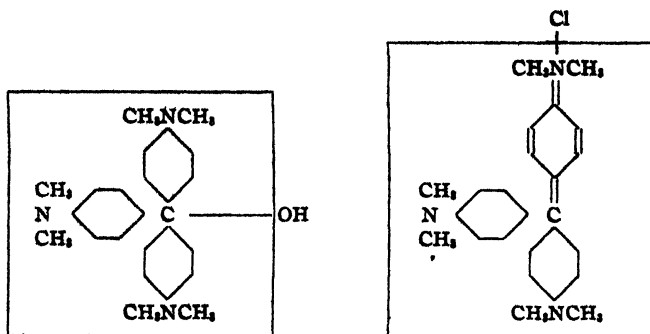
indicated by the addition of the symbol for hydrogen ion or for acid at the left or below the letter **R**. Thus a dichloride of crystal-violet would be represented by $\dfrac{\text{Cl}}{\text{ClHR}}$; a color-base dichloride, which would be colorless,

by $\begin{array}{c}\text{Cl}\\ \text{H}\\ \text{ClHR—OH}\end{array}$. The ions of such chlorides can all be represented by replacing the chlorines by positive charges. In the case of para-rosaniline, the symbol **R** would represent
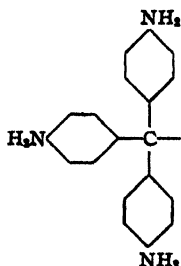
and for all the chromogens named above the same notation can be adopted.

As has been pointed out above, the changes in question are all to be attributed to reversible reactions of the chromogen with hydrogen ion, with hydroxyl ion, or with water. It will be well, at this point, to consider the constitution of the probable products of such reactions. Starting with the color-base of crystal-violet, ROH, which contains three nitrogens, there is the possibility of adding one, two, or three equivalents of hydrogen ion, to form the ions $\dfrac{\text{ROH}}{\text{H}^+}$, $\dfrac{\text{H}^+\text{ROH}}{\text{H}^+}$ and $\dfrac{\text{H}^+}{\dfrac{\text{H}^+\text{ROH}}{\text{H}^+}}$. Each of the four sub-

stances may lose hydroxyl ion, forming the ions R+, R+, H+R+, and
$$H^+ \qquad H^+$$
$$H^+$$
H+R+; the first three of these are in tautomeric equilibrium with the
$$H^+$$
colored (quinoid) ions $\overset{+}{R}$, $\overset{+}{R}$, and $H^+\overset{+}{R}$. Reactions with water will pro-
$$H^+ \qquad H^+$$
duce no changes which cannot be also brought about by reactions, successively, with hydrogen and hydroxyl ions. Owing to the symmetry of the crystal-violet molecule no isomers of these forms exist. The genetic relationship between these hypothetical substances is shown in Table I. In this table definite colors have been assigned to the three quinoid ions for reasons which will appear later.

TABLE I.

For a compound with one less amine nitrogen the substances in the bottom row of the table become impossible; with one amine nitrogen, only those in the first two rows remain; while triphenylcarbinol, having no nitrogen, is colorless under all conditions. On the other hand, molecular asymmetry, like that of rosaniline, increases the number of forms by the introduction of isomers.

Since the chromogens considered are amine carbinols, the relative speeds of the reactions postulated in Table I may be inferred from analogy with other amines and other carbinols. As is well known, salt formation from amines is instantaneous, whereas the reaction of carbinols with acids is invariably slow. Hence the reactions in Table I headed "loss of OH−" may be expected to be slow while all the others would be instantaneous.

The data needed for the establishment of the relative concentrations *of all* the substances present in acidic solutions of *N*-hexamethyl-*p*-trianilinomethyl chloride[1] fall naturally into two classes: the relative proportions of different colored substances in the solutions, and the variation of the proportions of colorless substances with the color of the solutions. The measurement of the proportions of substances of different colors involves comparisons of color intensities for many different shades lying between violet and yellow after equilibrium between all the different forms has established itself. On the other hand, since the hue of the solutions does not change on standing, the variation of the proportions of colorless substances in solutions of different colors involves only the measurement of the relation between original and equilibrium intensities.

The complete investigation is accordingly divided into three parts, the first to deal with the equilibrium between the colored forms; the second with the slow changes in color intensity toward equilibrium, and the third to comprise a discussion of the entire problem.

PART I.
Equilibrium between the Colored Forms of Crystal-Violet.

Acidic solutions of crystal-violet showed, on examination with a small spectroscope, well marked absorptions in the yellow, orange, and violet regions; the relative prominence of these absorptions changed in the order named above as the concentration of acid was increased. These facts were taken to mean that three substances, respectively violet, green, and yellow, produced the colors of all the solutions. This part of the present investigation was therefore undertaken to obtain quantitative proof of the truth or fallacy of the assumption of the presence of three, and only three, colored substances.

A 0.001 molal solution of crystal-violet (*N*-hexamethyl-*p*-trianilinomethyl chloride) was made in conductivity water and from this stock solution were made all the more dilute solutions used in the measurements. A 2 *N* solution of hydrochloric acid, standardized by titration against standard alkali, was used to obtain the desired concentrations of acid.

Since the color of freshly acidified crystal-violet solutions changes appreciably in the time required for a set of spectrophotometric measurements, it was necessary to make these measurements with solutions which had come to equilibrium. The ratios of initial to final color intensities in such solutions have been obtained from measurements[2] of the rate of

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[1] This substance was chosen rather than the pentamethyl derivative because it was available in (Kahlbaum's) pure form. Analysis gave N = 10.27%, 10.37%; theoretical, calculated for the hexamethyl derivative 10.33%; for the pentamethyl derivative, 10.70%.

[2] See Part II.

fading, and the absorption measurements at equilibrium have been combined with these ratios to obtain the initial absorption.

When monochromatic light of intensity I_o passes through an absorbing medium, the intensity of the transmitted light, I_1 is given by the relation:

$$I_1 = I_o \times 10^{-\epsilon d} \qquad (1)$$

where d is the depth of the absorbing layer and ϵ, the "extinction coefficient," is a constant which, for any wave length, is characteristic of the absorbing material. The value of the extinction coefficient for unit concentration of the absorbing substance is called the molecular extinction coefficient and is usually represented by A_λ. Then, in terms of this constant, equation (1) becomes

$$I_1 = I_o \times 10^{-A_\lambda Cd}$$

where C is the concentration in mols per liter of the absorbing substance, and the depth d, is measured in centimeters.

Equation (2) may also be written in the form,

$$\log I_1/I_o = A_\lambda Cd. \qquad (3)$$

The ratio of the intensity of the incident to that of the transmitted light was measured by means of a König, Martens and Grünbaum[1] spectrophotometer. In this instrument two beams of monochromatic light from the same source, which have passed respectively through the solution and through an equal column of the pure solvent, are polarized in mutually perpendicular planes and are compared by means of a Nicol in the rotating eye-piece of the instrument. If α be the angle at match between the analyzing Nicol and the polarizer in the beam from the pure solvent, then the ratio of the intensities is,

$$I_o/I_1 = \tan^2 \alpha, \qquad (4)$$

and combining with equation (3)

$$A_\lambda Cd = 2 \log \tan \alpha. \qquad (5)$$

It will be well at this point to consider the accuracy attainable with this type of instrument. Under favorable conditions of illumination the accuracy of setting is considerably greater than that of reading the angle between the Nicol prisms. The absolute magnitude of the latter is obviously the same at all angles, hence the maximum' of accuracy is reached when the specific extinction coefficient changes least rapidly with the angle, that is to say, when the logarithmic derivative of A_λ with respect to the angle is a minimum. From equation (5) this derivative is

$$\frac{d \ln A_\lambda}{d\alpha} = \frac{d \ln \tan \alpha}{\ln \tan \alpha \, d\alpha} = \frac{2}{\sin 2\alpha \cdot \ln \tan \alpha} \qquad (6)$$

and will be a minimum when its denominator is a maximum;

[1] Martens and Grünbaum, *Drude's Ann.*, 12, 984–1000 (1903).

$$\frac{d\,(\sin 2\alpha \ln \tan \alpha)}{d\alpha} = 2(\cos 2\alpha \ln \tan \alpha + 1) = 0. \qquad (7)$$

The solutions of this equation in the first quadrant are $\alpha = 16° \, 46'$; $\alpha = 73° \, 14'$. Substituting into equation (6), $\alpha = 16° \, 46'$, $d\alpha = 0.1°$ $= 0.0017$ radian; $d \ln A_\lambda = 1.2\%$; that is, the maximum accuracy is obtained if the concentration is so chosen that the instrument reading is $\alpha = 16° \, 46'$, and the error of a single reading, $0.1°$, will then produce an error of 1.2% in A_λ.

It should be further noted that the probable error in A_λ will be reduced nearly threefold by taking eight readings, as has been done in the measurements to follow. On the other hand, at the ends of the spectrum the lack of light makes the error in setting greater than that of reading α. The unavoidable inequality in illumination causes the value of α taken with the solution on the two sides of the instrument to differ, without introducing any error into their mean.

The Calibration of the Spectrophotometer.—The "wave length" scale of the spectrophotometer used being an entirely arbitrary one, it was necessary to calibrate it by means of some standard wave lengths. For this purpose were used the red lithium line, the sodium "D" line, and the yellow, yellow-green, blue-green and blue lines of mercury. All these lines appeared of appreciable width but had sharp edges, and therefore scale readings at both edges of the lines were made and their average was taken as the position of the line on the scale. No attempt has been made to correct for the slit width, since it was found that none of the slit widths used appreciably increased the apparent width of the lines. The results of the calibration measurements are given in Table II.

TABLE II.—THE CALIBRATION OF THE SPECTROPHOTOMETER.

Line.	Scale readings.			Slit width.	Wave length λ.	$\lambda^{-2} \times 10^8$.
	a.	b.	Mean.			
Li red	3388	3249		.		
	3387	3247		15 μ	6708 Å	2.222
	3387	3253	3318			
Na D	3080	2957		10		
	3080	2955		30	5890	2.880
	3090	2947	3018	30	5896	
Hg yellow	3038	2897		5	5790	
	3038	2896	2967	5	5769	2.995
Hg green	2862	2730		5		
	2862	2730	2976	5	5460	3.355
Hg blue-green	2467	2338		5		
	2471	2344	2405	10	4916	4.140
Hg blue	1840	1709		5		
	1841	1711	1777	5	4358	5.265

A ·calibration curve was drawn plotting instrument readings against the square of the frequencies, and from this curve were obtained the intermediate wave lengths corresponding to instrument readings.

TABLE III.—WAVE LENGTHS AND CORRESPONDING INSTRUMENT READINGS

Wave length λ	Instrument readings.	Wave length λ.	Instrument readings.
4609 Å	2100	5955 Å	3050
4800	2300	6073	3100
5025	2500	6215	3150
5295	2700	6348	3200
5636	2900	6650	3300
5839	3000		

In Table III are given the wave lengths and the corresponding instrument readings at which all absorption coefficients were measured.

The Spectrophotometric Measurements.—The molecular extinction coefficient, A_λ, which has been defined in equation (2) is, according to Beer's law, a constant with respect to the concentration whenever dilution does not affect the chemical nature of the colored substances. That Beer's law holds for the solutions used in this work follows from the fact that the decrease in color intensity to an equilibrium value is unaccompanied by change of hue. Hence it is clear that comparison between the absorptions of solutions of different chromogen concentrations is possible through the use of the molecular extinction coefficient, and since the measurements gave the angle α of equation (5), this equation is directly applicable for the calculation of this characteristic constant. It may be pointed out again that the angle α was measured with a 10 cm. tube of the solution of chromogen on one side of the instrument and a 10 cm. tube of pure solvent on the other; and that after settings had been made in all four quadrants the tubes were interchanged and settings were again made in four quadrants. Thus any inequality in the illumination was eliminated from the average value of the angle. The method by which the calculation was made is illustrated, using a typical set of eight instrument readings, in Table IV

TABLE IV —INSTRUMENT READINGS AND CALCULATIONS ON THE BLUE SOLUTION FOR WAVE LENGTH 5955 Å.

Concentration of chromogen $= 5.0 \times 10^{-4}$ m.
Concentration of HCl $= 0.016$ N.

Quad.	I.	II	III	IV.		4α	α.
L	72 1°	105 9°	252.1°	285 8°	360° + I — II + III — IV	$= 292\ 5°$	73 12°
R... ...	16 4°	161.6°	196.5°	341.4°	— I + II — III + IV	$= 290.1°$	72.52°
						Mean,	72 82°

$A_\lambda = 2 \log \tan 72.82° + (10^{\text{cm.}}) + (5\ 0 \times 10^{-4}\ \text{m.}) = 20400.$

"L" and "R" signify respectively "chromogen solution on left side of instrument" and "chromogen solution on right side of instrument."

In the same way the values of α were obtained at the eleven wave lengths given in Table III for all six solutions, and these values of α, together with the concentrations of the solutions and the wave lengths to which they refer are given in Table V. From the mean values of α, A_λ has been calculated to obtain a measure for the concentrations of the colored substances, and Table VI gives these values of A_λ.

Dividing these figures by the ratio of equilibrium to initial color intensity (γ), found in Part II, we obtain the initial values of the molecular extinction coefficient. These values are given in Table VII.

TABLE V —VALUE OF THE ANGLE α FOR SOLUTIONS OF THE CHROMOGEN IN PURE WATER AND IN ACID

Color	Violet	Violet-blue	Blue	Blue-green	Yellow-green	Green-yellow
Conc HCl	None	0 004 N	0 016 N	0 040 N	0 20 N.	1.00 N
Conc chromogen	1 5 × 10^{-6}	2 0 × 10^{-6}	5 0 × 10^{-6}	20 × 10^{-6}	50 × 10^{-6}	50 × 10^{-6}
Wave length						
6650 Å	46 80°	51 52°	56 30°	59 28°	50 38°	47.05°
	46 08°	51 55°	55 10°	59 20°	51 42°	48 15°
6348	52 15°	61 12°	70 25°	78 50°	59 92°	47 92°
	51 88°	61 65°	69 75°	78 58°	59 20°	49 10°
6215	60 50°	67 72°	71 95°	78 58°	59 52°	47 72°
	59 88°	68 12°	71 55°	79 00°	58 80°	48 78°
6073	70 82°	72 88°	72 72°	76 68°	55 35°	47 20°
	70 30°	73 38°	72 00°	76 70°	57 08°	48 10°
5955	77 18°	77 38°	73 12°	74 60°	53 25°	46 90°
	77 12°	77 20°	72 52°	74 92°	55 12°	47 82°
5830	77 58°	77 52°	71 88°	72 10°	52 05°	46 32°
	77 22°	77 08°	71 08°	73 18°	53 78°	47 05°
5636	72 78°	72 82°	65 65°	65 00°	49 00°	46 68°
	73 18°	72 52°	65 10°	66 28°	51 38°	47 10°
5295	66 80°	65 50°	57 78°	55 58°	46 50°	47 00°
	67 18°	65 15°	57 25°	57 70°	49 65°	46 95°
5025	56 10°	55 32°	51 05°	49 88°	46 28°	48 58°
	56 25°	55 02°	50 22°	52 58°	50 48°	48 32°
4800	51 20°	49 62°	48 28°	48 52°	46 95°	50 85°
	51 70°	49 18°	47 52°	51 10°	51 82°	50 90°
4609	47 80°	47 08°	47 20°	48 82°	49 70°	54 45°
	49 65°	47 22°	46 55°	51 35°	53 98°	53 85°

The set of values of the molecular extinction coefficient at various wave lengths for a single chemical species of the chromogen will be called a "fundamental" The absorption of a solution containing several chemical species will be the sum of the products of the fundamentals by the fractions of chromogen present in the respective colored forms. To prove that three colored forms are present we must show that three fundamentals

TABLE VI —EQUILIBRIUM VALUES OF THE MOLECULAR EXTINCTION COEFFICIENT Aλ AT 20 0°

Color	Violet	Violet blue	Blue	Blue green	Yellow green	Green yellow
Conc. HCl	None	0 004 N	0 016 N	0 040 N	0 20 N	1 00 N
Conc chromogen	1 5 × 10⁻⁶	2 0 × 10⁻⁶	5 0 × 10⁻⁶	20 × 10⁻⁶	50 × 10⁻⁶	50 × 10⁻⁶

<p>$\bar{A}_\lambda \times 10^3$</p>

Wave length						
6650 Å	2 90	9 99	6 64	2 25	0 390	0 155
6348	14 51	26 31	17 56	6 93	0 964	0 214
6215	32 22	39 18	19 27	7 09	1 00	0 198
6073	60 19	52 06	19 91	6 26	0 709	0 161
5955	85 60	64 65	20 41	5 65	0 565	0 144
5830	86 79	64 71	18 99	5 05	0 493	0 097
5636	68 55	50 57	13 55	3 43	0 316	0 114
5295	49 62	33 76	7 83	1 81	0 186	0 120
5025	23 20	15 75	3 54	0 950	0 204	0 210
4800	13 14	6 70	1 76	0 734	0 268	0 398
4609	7 53	3 26	1 13	0 777	0 418	0 564

TABLE VII —INITIAL VALUES OF THE MOLECULAR EXTINCTION COEFFICIENT, Aλ AT 20 0°

<p>$A_\lambda \times 10^4$</p>

Wave length						
6650 Å	0 29	1 20	2 80	1 88	1 12	0 35
6348	1 45	3 16	5 84	5 78	2 79	0 47
6215	3 22	4 70	6 40	5 91	2 37	0 44
6073	6 02	6 25	6 62	5 -2	2 04	0 36
5955	8 56	7 76	6 79	4 71	1 68	0 32
5830	8 68	7 77	6 43	4 21	1 42	0 22
5636	6 86	6 06	4 50	2 86	0 91	0 25
5295	4 96	4 05	2 60	1 51	0 54	0 27
5025	2 32	1 89	1 18	0 79	0 59	0 46
4800	1 31	0 80	0 58	0 61	0 77	0 38
4609	0 75	0 39	0 38	0 65	1 20	1 25

are necessary and sufficient. The calculation of the fundamentals from the absorptions of mixtures of forms is *algebraically* impossible However, if we impose the restrictions that the concentration of total chromogen is fixed, and that neither the concentration of any of the forms not their absorptions at any wave length can become less than zero, the fundamentals are restricted within very narrow limits

It was at first attempted to assume that the sum of the fractions of chromogen in the several colored forms added up to unity, but this was found impossible, indicating that even initially a part of the chromogen is present is some colorless form. However, this sum cannot exceed unity and this condition was imposed

The fundamentals were found by trial, and are given in Table VIII and Fig. 1.

The fractions of chromogen present in the different forms are given in Table IX.
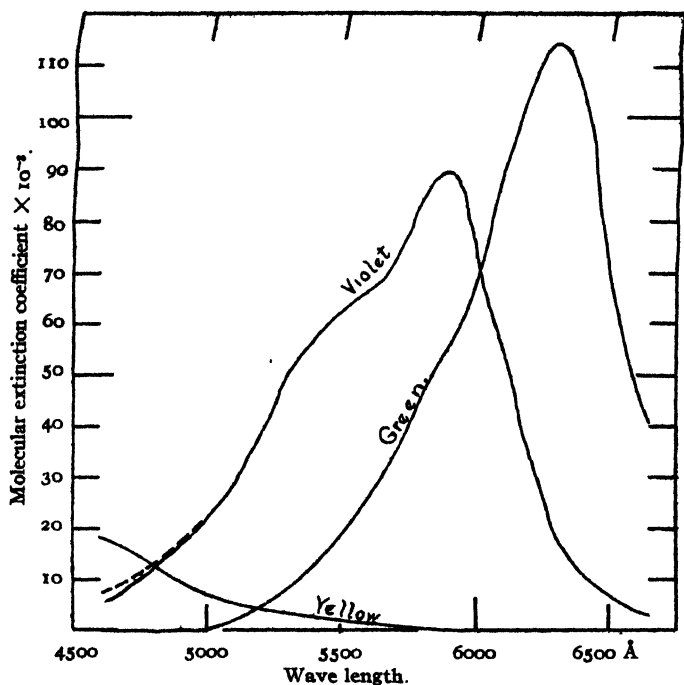
Fig. 1.—Fundamental absorption curves of crystal-violet.

TABLE VIII.—FUNDAMENTAL MOLECULAR EXTINCTION COEFFICIENTS.

Wave length.	Violet.	Green.	Yellow.
6650 Å....................	3000	40800	...
6348........................	14500	112500	...
6215........................	32200	107200	...
6073........................	60200	82500	...
5955........................	85600	61000	...
5830........................	86800	49200	200
5636........................	68400	28400	1300
5295........................	49600	8000	3500
5025........................	23200	800	6700
4800........................	12000	..	12800
4609........................	5000	..	18300

TABLE IX.—CALCULATED FRACTIONAL CONCENTRATIONS OF COLORED FORMS.

Color of solution.	Acid.	Violet.	Green.	Yellow.	C by diff.
Violet.....................	None	1.000	...	...	..
Violet-blue..............	0.004 N	0.779	0.195	0.011	..
Blue.....................	0.016 N	0.462	0.466	0.090	..
Blue-green..............	0.040 N	0.206	0.490	0.298	..
Yellow-green....:.......	0.20 N	0.019	0.250	0.690	0.04
Green-yellow............	1.00 N	0.003	0.042	0.685	0.27

The comparison with the experimental results is given in Figs. 2 and 3, on which the lines represent the calculated absorptions, while the experimental points are marked by crosses. The completeness of the agreement establishes that three absorbing substances are necessary and sufficient to
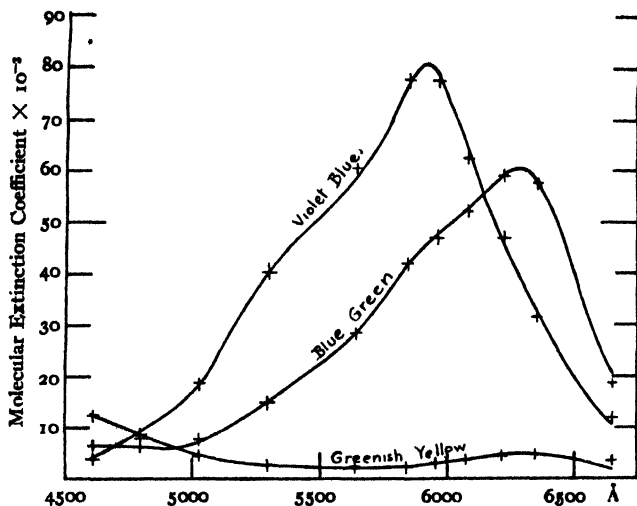
Fig. 2.—Absorption curves for crystal-violet.
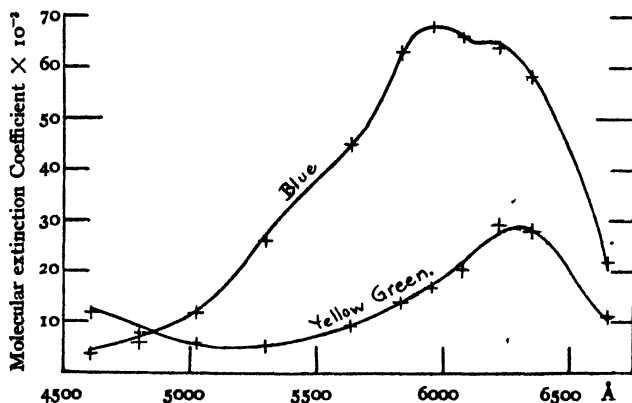
Fig. 3.—Absorption curves for crystal-violet.

produce the observed absorption of all the solutions. The presence of other colored substances would be possible only if their absorption were a linear function of that of two or all three of the fundamentals given above— a condition so improbable as to merit practically no consideration.

Such conclusions as are possible will now be drawn regarding the nature of the substances *initially* present in acidic solutions of crystal-violet. It is well known that the color of strong electrolytes is almost completely independent of the degree of ionization. The work of Hantzsch and others has shown that pseudo-bases, such as crystal-violet, *are* strong electrolytes in acid solution; hence the concentrations of colored forms found by colorimetric means are the sums of ionized and unionized forms. The researches of A. A. Noyes and his co-workers have shown that if γ_1 be the degree of ionization of a uni-univalent strong electrolyte in a solution of total ion-concentration C_1, then the degree of ionization, γ_{mn}, of a salt of valence product mn is equal to γ_1^{mn}. If now the ions of two chlorides ACl_p and BCl_q combine to form a $(p+q)$-valent ion the equilibrium constant for the reaction $AB^{[p+q]+} = A^{p+} + B^{q+}$ is

$$K = \frac{(A^{p+})(B^{q+})}{(AB^{[p+q]+})} = \frac{(\Sigma A)\gamma_1^p(\Sigma B)\gamma_1^q}{(\Sigma AB)\gamma_1^{p+q}} = \frac{(\Sigma A)(\Sigma B)}{(\Sigma AB)}$$

where (ΣA), (ΣB) and (ΣAB) are the total concentrations of ionized or un-ionized ACl_p, BCl_q and $ABCl_{p+q}$ Hence the equilibrium constant for the ions is identical with that for the total reagents, and mass-law considerations can be applied to the total concentrations in such reactions, of which those of crystal-violet with hydrochloric acid are typical cases. The solid violet substance is known to be $C_{25}H_{30}N_3Cl$, which, for brevity may be written RCl, hence it may be concluded that the violet fundamental is due to $RCl \rightleftharpoons R^+ + Cl^-$, while the increase in the concentrations, relative to it, of the other colored forms with increasing acid concentration proves that they are formed from it by combination with acid. The amount of acid can be found by application of the mass law.   In Table X are given values of the ratios $K_1 = \dfrac{(\Sigma V)(\Sigma H)}{(\Sigma G)}$, $K_2 = \dfrac{(\Sigma G)(\Sigma H)}{(\Sigma Y)}$, $K_3 = \dfrac{(\Sigma Y)(\Sigma H)}{(\Sigma C)}$, where (ΣV), (ΣG), (ΣY) and (ΣC) are the respective total concentrations of violet, green, yellow and initial colorless forms, and (ΣH) is the total acid concentration.

TABLE X —MASS LAW CONSTANTS

Color of solution	Acid	K_1	K_2	K_3
Violet-blue	0 004 N	0 0160		
Blue	0 016 N	0 0159	0 083	
Blue-green	0 040 N	0 0168	0 066	
Yellow-green	0 200 N	0 0152	0 072	3 4
Green-yellow	1 000 N		0 061	2 5

The substantial constancy of the first two ratios establishes the composition of the green and yellow forms as $RHCl_2 \rightleftharpoons RH^{++} + 2Cl^-$ and $RH_2Cl_3 \rightleftharpoons RH_2^{+++} + 3Cl^-$, respectively.   There is also evidence,

not entirely conclusive, that the "initial colorless" form is $RH_3Cl_4 \rightleftharpoons RH_5^{++++} + 4Cl^-$.

PART II.

Measurements of the Rate of Fading of Crystal-Violet in Acid Solution.

The slow changes in color intensity mentioned in the introduction take place at a rate and to an extent which increase with increasing acid concentration. With acid concentrations less than 0.0001 N no measurable fading occurs, while in normal acid the color fades rapidly and nearly disappears in the course of an hour. Miss A. Morse and Miss L. Vance, at the suggestion of Prof. H. C. Biddle, carried on an investigation of this fading, using a Stammer colorimeter. They demonstrated that the reactions involved are monomolecular in both directions and also found a much greater dependence on temperature than had been anticipated. The measurements were therefore repeated at 20.0°, using the instrument and concentrations of solutions employed in Part I of this investigation.

Constancy of temperature during the measurements was maintained by setting up the spectrophotometer in an air thermostat which was maintained at 20° ± 0.1° by means of an electric lamp. The entire equipment was placed directly over a large water thermostat constant at 20° ± 0.01, in which all solutions, tubes, etc., were permitted to come to constant temperature before the beginning of an experiment. The large heat capacity of the solutions must have prevented their following to any great extent the small and rapid fluctuations in the temperature of the air thermostat.

The reactions which produce colorless modifications of the chromogen from colored ones all take place in solutions extremely dilute with respect to chromogen, and so the only concentrations which can be changed appreciably are those of the colored and colorless substances. The reaction may therefore be represented as "colored $\rightleftharpoons$ colorless;" and if, now, it be assumed that this reaction is monomolecular in both directions, the rate of the transformation of colored to colorless chromogen is expressed by the differential equation

$$- dC/dt = K_1C - K_2L, \qquad (8)$$

where C and L are the concentrations at the time "t" of the colored and of the colorless substances, and K_1 and K_2 are the specific reaction rates of the direct and reverse reactions. Representing the initial concentration of chromogen by C_0, the values of C and L become $C_0\gamma$, and $C_0(1-\gamma)$, and equation (8) then reads

$$-d\gamma/dt = K_1\gamma - K_2(1-\gamma), \qquad (9)$$

an equation giving the rate of change of γ, the fraction of chromogen which is colored. On integration this last equation becomes

$$\ln (\gamma/\gamma_\infty - 1) = -(K_1 + K_2)t + \ln (1 - \gamma_\infty) \qquad (10)$$

or

$$\ln (C - C_\infty) = -(K_1 + K_2)t + \ln (C_0 - C_\infty). \qquad (11)$$

Changing to common logarithms and combining with equation (5) gives the two equations

$$\log (\log \tan \alpha - \log \tan \alpha_\infty) = \frac{-K_1 + K_2}{2.303} t +$$
$$\log (\log \tan \alpha_0 - \log \tan \alpha_\infty). \qquad (12)$$

$$\gamma_\infty = \frac{\log \tan \alpha_\infty}{\log \tan \alpha_0}. \qquad (13)$$

At equilibrium equation (9) becomes, $K_1\gamma_\infty - K_2(1 - \gamma_\infty) = 0$, whence

$$K_2 = \gamma_\infty (K_1 + K_2), \qquad (14)$$

an equation by which the separate specific reaction rates may be calculated.

It follows that if $\log (\log \tan \alpha - \log \tan \alpha_\infty)$ be plotted against the time there should result a straight line whose slope is $(K_1 + K_2)/2.303$ and from whose intercept γ_∞ may be calculated by equation (13).

From equation (7) it may be inferred that the accuracy of the measurements suffers if α varies too widely from $74°$ (or the corresponding angle in the other half quadrants). The wave lengths at which rate measurements were made were so chosen as to give as high an accuracy as possible, hence in the more acid solutions a change to another wave length was made when the absorption of the solution became too small. The observed values of α are given in Table XI.

The mode of calculating the average value of α used in Part I automatically eliminates two sources of error of single measurements: that due to the angle between the zero of the scale and the position of crossing of the Nicol prisms (found to be $1.1°$), and that due to inequality of illumination of the two sides of the spectrophotometer. To make the first correction, $1.1°$ was added to all the observed angles before taking the logarithmic tangent; to make the second, $0.1°$ has been added to left-hand readings and subtracted from right-hand readings in the case of the violet-blue solution. In the other cases the correction has been made either by averaging equal numbers of right-hand and left-hand observations or by drawing the best representative line of the plot midway between those determined by the two sets of readings.

Since in the more slowly changing solutions several minutes are required to produce a change of $0.1°$ in α, in these cases two or more readings have been reduced to the same half quadrant and averaged before taking logarithmic tangents, and the times of readings likewise averaged.

TABLE XI.—AVERAGE VALUE OF α REDUCED TO SECOND HALF-QUADRANT.

Color.	Violet-blue.		Blue.		Blue-green.		Yellow-green.		Green-yellow.	
Conc. HCl	0.004 N.		0.016 N.		0.040 N.		0.20 N.		1.00 N.	
Conc. chromogen	2.0×10^{-6} m.		5.0×10^{-6} m.		20×10^{-6} m.		50×10^{-6} m.		50×10^{-6} m.	
	Mean Time. Min. Sec.	Mean α. λ 5839.	Mean Time. Min. Sec.	Mean α. λ 5295.	Mean Time. Min. Sec.	Mean α. λ 5025.	Mean Time. Min. Sec.	Mean α. λ 5295.	Mean Time. Min. Sec.	Mean α. λ 3839.
	5	80.4°	5	76 6°	1	79.5°	3^{30}	84.1	3	70.4°
	8	80.3	7	76.6	4	78 6	4	83 6	4	68.2
	10	80.1	9	76.2	6	77.7	5	82.5	5	67.8
	37	79.4	13	75.7	8	77.5	6	81 1	6	65.7
	41	79.5	17	75.4	29	70.6	7	80 8	7	65.2
	70	78.8	21	74.8	32	69.7	8	79 5	8	63.0
	71^{30}	78.9	25	74.0	35	69.2	9	76.3	9	62.9
	105	78.3	29	73.4	43	66.2	10	76.7	10	61.4
	106^{30}	78.3	33	72.9	45	66.1	11	75.7	∞	46.60
	120^{30}	77.9	39	72.0	46^{30}	65.8	12	75.0		
	122^{30}	78.1	47	71.4	∞	51 22	13	74 1	λ 6348	
	124^{30}	78.0	55	70.5	λ 5295		14^{18}	72.6	12^{30}	71.5
	126	78.0	63	69.6	38^{30}	81.1°	15	71.0	13	70.6
	∞	77.18	73	68.5	40^{30}	80.7	16	70.0	14^{30}	67.9
			81	67.8	41^{30}	80.3	17	68 1	15	67.7
			91	67.0	48	78.9	18	67.9	16	66.4
			∞	57.50	49^{30}	78.3	∞	48.0/	17	65.0
					68	73.8	λ 5636		18	64.5
					69^{30}	72.9	16^{40}	82.7	19	62.0
					72^{30}	72.1	17^{30}	81.8	20	61.0
					75	72.3	18^{30}	80.9	22	59.1
					∞	56.63	19	80.9	27	55.8
							20	79.6	28	56 2
							21	78.1	∞	47.65
							22	77.0		
							29	69 2		
							30	69.0		
							38	62.1		
							39	61.6		
							∞	50.19		
							λ 6073			
							37	78.2		
							38^{30}	76.4		
							39^{30}	75.2		
							40^{30}	74.4		
							41^{30}	73 7		
							42	73.1		
							56	63.8		
							58	62.8		
							60	61.8		
							∞	56.20		

TABLE XII.—CALCULATIONS FROM RATE DATA ON BLUE-VIOLET SOLUTION (TAKEN AT $\lambda = 5839$ Å)

No. of readings	Mean time	Mean α	log tan α	$lt\alpha - lt\alpha_\infty$	log Δ
7	5	80 4	0 7718	0 1247	9 0959
4	8	80 3	0 7672	0 1201	9 0795
4	10	80 1	0 7581	0 1110	9 0453
4	37	79 4	0 7278	0 0807	8 9069
4	41	79 5	0 7320	0 0849	8 9289
4	70	78 8	0 7033	0 0562	8 7497
4	71³⁰	78 9	0 7073	0 0602	8 7796
4	105	78 3	0 6838	0 0367	8 5647
4	106³⁰	78 3	0 6838	0 0367	8 5647
4	120³⁰	77 9	0 6688	0 0217	8 3365
4	122³⁰	78 1	0 6763	0 0292	8 4654
4	124³⁰	78 0	0 6725	0 0254	8 4048
4	126	78 0	0 6725	0 0254	8 4048
	∞	77 18	0 6471		
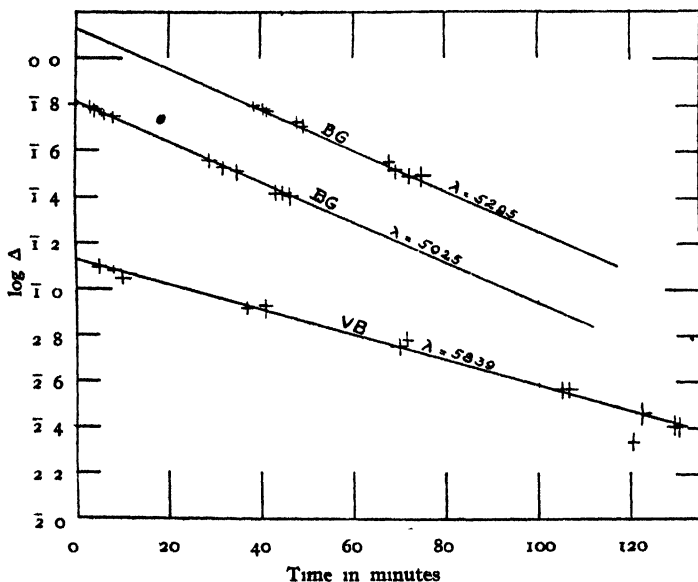
Fig 4

The calculation of the left-hand member of equation (12) is given for the violet-blue solution in Table XII, in which the first column gives the number of readings averaged, the second and third columns the average time and average α, the fourth column gives log tan α, the fifth log tan α—log tan α_∞ and the sixth log (log tan α — log tan α_∞), which has been called log Δ. The values of α_∞ are taken from Part I, Table V The

calculations from the other solutions were made in the same way. The results of these calculations are shown graphically on Figs. 4 to 7.
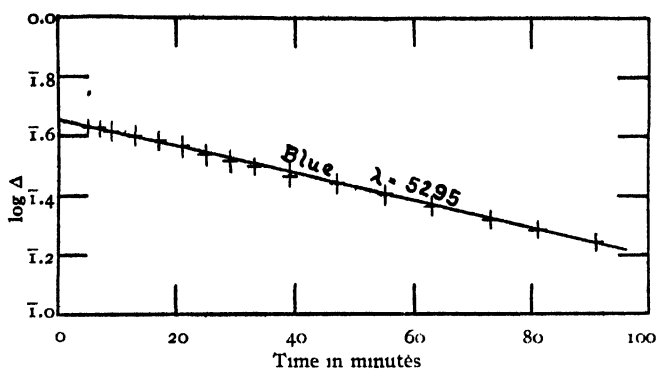
Fig 5
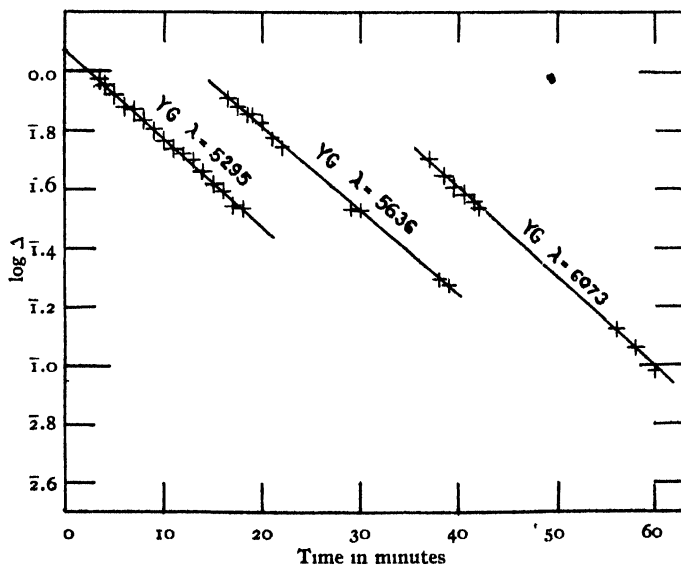
Fig 6

Table XIII gives in the first two columns the intercept and slope of the lines of these plots, in Column three the values of γ_∞ calculated by equations (12) and (13), and in Column five the value of K_2 from equation (14). K_1 is obtained by difference and is given in Column four.

The effect of increasing acid concentration on the rates of the reactions

"colored $\rightleftarrows$ colorless" is to cause the rate of the direct reaction to increase continuously although not proportionately, and the rate of the reverse reaction to pass through a minimum.

TABLE XIII.

Color.	$(K_1+K_2)/2.303.$ Mean slope.	Intercept.	γ_∞.	K_1.	K_2.
Violet-blue...............	0.00525	$\bar{1}.113$	0.838	0.00202	0.0101
Blue.....................	0.00456	$\bar{1}.657$	0.301	0.0073	0.00316
Blue-green..............	0.00874	$\begin{cases}\bar{1}.817 \\ 0.124^1\end{cases}$	0.120	0.0177	0.00241
Yellow-green.............	0.0295	$\begin{cases}0.072 \\ 0.384^2\end{cases}$	0.0348	0.0656	0.00237
Green-yellow............	0.0350	$\bar{1}.716^3$	0.0452	0.0768	0.00364
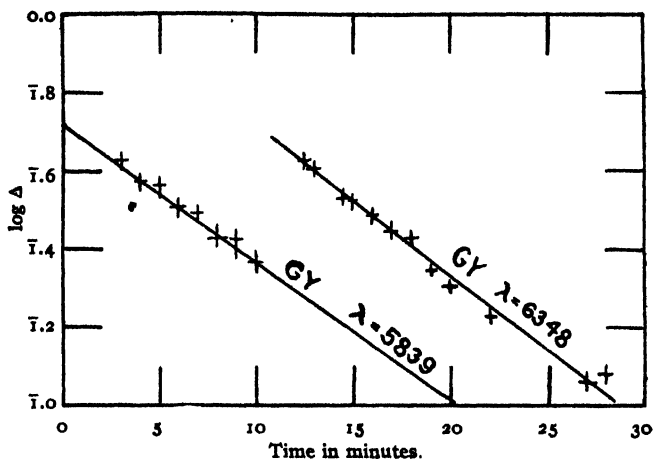
Fig. 7.

PART III.

Discussion.

The composition of the colored ions has been definitely established in Part I. Comparison with Table I shows that they are to be identified with the three quinoid ions there given, and since they are in rapid tautomeric equilibrium with three of the benzoid ions the concentrations given in Table IX are the sum of the concentrations of the two tautomers, and there appears to be no way of ascertaining the separate concentrations.

The carbinol forms, like the benzoid ions above, are colorless, hence the measurement of their concentrations must of necessity be indirect. The

[1] γ_∞ has been calculated from this intercept ($\lambda = 5295$) since readings at the shorter wave length ($\lambda = 5025$) were less reliable.

[2] γ_∞ has been calculated using both intercepts ($\lambda5295$, $\lambda5636$).

[3] $\lambda = 5839$.

study by Hantzsch and others of the equilibrium between carbinol, violet ion and hydroxyl ion in alkaline solutions, shows that the concentration of carbinol becomes very small in neutral solution; it is *a fortiori* negligible in acidic solutions. The concentration of the ion $\dfrac{ROH}{H^+}$ may be inferred from the rates of reaction in neutral solution in the two directions. The rate of fading, K_1, from Table XIII, is 0.002 min.$^{-1}$ in 0.004 N acid and is presumably still less in neutral solution, whereas Biddle[1] has found the rate of the *reverse* reaction in neutral solution too great to measure. It may therefore be concluded that at equilibrium the carbinol ion concentration is certainly less than 0.1% and probably less than 0 01%, and when the violet ion concentration is diminished by acidification will decrease in the same ratio. From the definition of γ_∞ (see equation (10)) it follows that $(1/\gamma_\infty - 1)/(Y)$ is the ratio of *total* carbinol concentration to the concentration of yellow ion (plus its tautomer); the values of this ratio are given in Table XIV.

TABLE XIV

Color of solution	(HCl)	(Y)	$(1/\gamma_\infty-1)/(Y)$	$K_1/(Y)$
Violet-blue . . .	0 004 N	0 011	18	[0 184]
Blue .	0 016	0 090	25 8	0 081
Blue-green	0 040	0 298	24 6	0 060
Yellow-green	0 20	0 690	41 6	0 097
Green-yellow .	1 00	0 685	32 3	0 112

The ratio will be seen to be fairly constant, increasing slightly[2] with increase in acid concentration. This is evidence that the carbinol $\dfrac{H^+ROH}{H^+}$ is the principal colorless form in strongly acidic solutions. As for the compound $\dfrac{H^+ROH}{H^+}$ we know only that its concentration at equilibrium is never large, although it may constitute, in some solutions, a large part of the total carbinol.

It is also possible to draw some conclusions as to the rates of the various reactions. The reaction $ROH \longrightarrow R^+ + OH^-$ is very rapid, as has been mentioned above; the reverse reaction takes place rapidly is strong alkali. The observation of Biddle[1] that the rate of development of color in solutions of the carbinol between neutrality and 0.01 N acid is given by the formula $A + B/(\Sigma H)^2$ indicates that the reaction proceeds at a rate, A, unaffected by the acid concentration, increased by a rate $B/(\Sigma H)H^2$ where

[1] *Loc. cit.*

[2] If any importance is to be attached to this increase it is evidence that compounds exist containing more H^+ than the carbinol $\dfrac{H^+ROH}{H^+}$

(ZH) is the acid concentration. The second term is to be attributed to the reaction $ROH \longrightarrow R^+ + OH^-$; for the formula holds in a region where the rate of reaction due to the carbinol is considerable, and so must be one of the terms, and this term must also diminish with increasing concentration of hydrogen ion since the carbinol concentration does so. Then the first term in the formula must be identified with the rate of the reaction $H^+ROH \longrightarrow H^+R+ + OH^-$, in order to account for the presence of the

$$H^+ROH \longrightarrow H^+R+ + OH^-$$
$$H+ \qquad\qquad H^+$$

inverse square of the acid concentration in the second term. It is also necessary that the ion H^+ROH constitute the largest part of the total

$$H^+$$

carbinol concentration, for otherwise the first term would also be a function of the acid concentration. Since the rate of the reverse reaction, K_2 (see Table XIII) continues to increase after the concentration of green, and therefore of H^+ROH, has reached a maximum it must be concluded

$$H^+$$
$$H^+$$

that the reaction
$$H^+ROH \longrightarrow H^+R+ + OH^-$$
$$H^+ \qquad\qquad H^+$$

is also taking place.

The last column of Table XIV gives the ratio of K_1 to the concentration of yellow. The approximate constancy of this ratio shows that the reaction

$$H^+ \qquad\qquad\qquad H^+$$
$$H^+R+ + OH^- \longrightarrow H^+ROH \quad \text{(or the equivalent } H^+R+ + H_2O \longrightarrow$$
$$H^+ \qquad\qquad H^+ \qquad\qquad\qquad\qquad\qquad H^+$$
$$H^+$$
$$H^+ROH) \text{ is the principal one taking place in acidic solutions.}$$
$$H^+$$

In conclusion, a few words as to the relation between the color and constitution of crystal-violet will not be out of place. From the electromagnetic theory, absorption of light can result only from the sympathetic vibration of charged particles. These particles may be either electrons or ions, and the study of the ultraviolet and infra-red absorptions of such substances as quartz, rock salt, water and carbon dioxide, has shown that resonance periods in the former region are in general due to electrons, in the latter to charged radicals. Resonance periods in the visible spectrum may therefore be due either to ions vibrating at a frequency unusually high or to electrons of unusually low frequency. The latter condition might be expected in an ion in which tautomeric shift would involve the virtual passage of an electron from one end of the ionic structure to the other. Thus phenolphthalein, which Wegscheider[1] and Rosenstein[2] have

[1] R. Wegscheider, Z. Electrochem., 14, 510 (1908).

[2] L. Rosenstein, This Journal, 34, 1117 (1912); L. Rosenstein and E. Q. Adams, Ibid., 35, 1883 (1913).

shown to assume color only when the dibasic ion is formed, has then the structure

 which can become
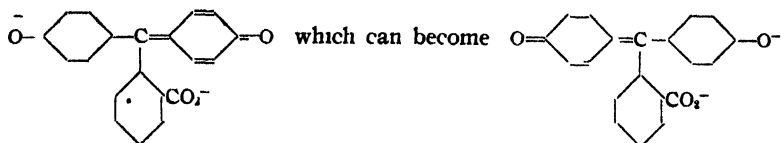
by the type of transformation just mentioned Continuous alternation between the two forms is equivalent to the oscillation of a single electron between the positions The frequency of such an oscillation might be expected to be less than that of an electron limited in its motion to the dimensions of a single atom, and therefore to give an absorption band in the visible rather than in the ultraviolet In the case of crystal violet a similar relation exists between the ions $\overset{-}{R}$, $+R$ and R, and between $\overset{+}{R}$ and $+R$, and both these forms, as has been experimentally shown, have great H^+ absorbing power The much weaker color of the yellow ion can be accounted for by its quinoid structure which is capable of producing a yellow color even where no electronic shift beyond a single benzene ring seems possible

Rosaniline and para rosaniline give ions which are similar to those of crystal violet and may be represented by the same symbols It is therefore to be expected that the rosanilines would have the same number of absorption bands as crystal violet and the relative position of the three is indeed found to be the same The first two absorption bands are, however, much closer together, so that on casual observation the first two colors are hardly distinguishable In the case of malachite green (which has two amine nitrogens) only the ions $\overset{+}{R}$ and $+R$ are related as indicated above, it therefore should have only the two last colors of crystal violet, and such is again the case The interesting and important problem remains to apply similar considerations to other derivatives of triphenyl methane and related substances

BERKELEY CAL

CERTAIN DERIVATIVES OF IODOANIL.[1]

By C LORING JACKSON AND E K BOLTON
Received April 23 1914

This paper contains a description of the conclusion of our work upon

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton

the derivatives of iodoanil, which was taken up by one of us (B.) at the suggestion of Professor H. A. Torrey in continuation of his work with Hunter.[1] After the preparation of the diiododimethoxyquinone, diiododiethoxyquinone and silver iodoanilate, Professor Torrey's lamented death made a new arrangement necessary, and accordingly the rest of the work has been carried on by us together.

We have already described[2] the most striking cases in which iodoanil behaves differently from chloro- or bromoanil. The substances described in this paper show a surprising resemblance to the corresponding chlorine or bromine compounds; the color, for instance, is essentially the same, although, in other cases, iodine has shown a marked tendency to deepen color, and no qualitative difference was observed in the solubilities. Torrey and Hunter[1] found, with the dihalogendiphenoxyquinones, that the melting point of the bromine compound lay half way between those of the chlorine and iodine compounds, and that the same was true of the cresoxy derivatives. In the hope of finding similar regularities, we have prepared several series of dihalogenquinones, the melting points of which are given below:

	$C_6X_2(CH_3O)_2O_2$.	$C_6X_2(C_2H_5O)_2O_2$.	$C_6X_2(C_7H_7O)_2O_2$.
Cl	141–2°²	104–5°³	142°⁴
Br	175°⁴	139°⁵	146°
I	196°	186°	160°

	$C_6X_2(C_3H_7O)_2O_2$.	$C_6X_2(CH(COOC_2H_5)_2)_2O_2$.
Cl	182.5°⁷	132°⁸
Br	205°	109°
I	207°	138°

The only approach to regularity in these melting points is found in the alkyloxy compounds, and here the differences from the expected melting points ($+7°$ and $-5°$) are too great for us to admit the existence of such a regularity. In the dimalonic ester quinones, the melting point of the bromine compound is even lower than that of the chlorine derivative. These data, therefore, indicate that the relation of the melting points observed by Torrey and Hunter is a special case and not part of a general law applying to all quinones containing halogens.

The derivatives mentioned above, with the exception of the diaceto compounds, were made by the action of the reagent on the diiododiphen-

[1] THIS JOURNAL, **34**, 702 (1912).

[2] "Octoiodoquinhydrone," THIS JOURNAL, **36**, 301 (1914); "Action of Alkaline Hydroxides on Iodoanil," THIS JOURNAL, **36**, 551 (1914).

[3] Kehrmann, *J. prakt. Chem.*, **40**, 365 (1889).

[4] Will, *Ber.*, **21**, 608 (1888).

[5] Bentley, *Am. Chem. J.*, **20**, 479 (1898).

[6] Jackson, Oenslager, *Ibid.*, **18**, 12 (1896).

[7] Nef, *J. prakt. Chem.*, **42**, 170 (1890).

[8] Stieglitz, *Am. Chem. J.*, **13**, 38 (1891).

oxyquinone, since we found, as with the chlorine derivatives,[1] that in this case the reaction ran smoothly with an almost quantitative yield, whereas, if the reagent acted directly on the iodoanil, the yields were small and the product hard to purify. The diiododianilinoquinone, melting with decomposition at 240° (uncor.), and the diiododi-p-toluidinoquinone decomposing at 205° (uncor.) were also prepared in this way. In making the dimethoxy- and diethoxy-compounds the first products were the corresponding diiododialkyloxyquinone hemiacetals, which dropped into the quinones, when heated for a short time with acetic anhydride. This is worth noting, since the dichlorodimethoxy-p-quinone dimethylhemiacetal is decomposed in the same way,[1] indicating that the hemiacetals of the para series are less stable than those derived from the o-quinones, which, to judge from four examples, are not decomposed by acetic anhydride; but give acetyl derivatives, if monohemiacetals,[2] or show no action in the case of the one dihemiacetal[3] we can find.

In making the benzyloxy compound, alcohol must be carefully excluded. On one occasion, when dried but unwashed ether was used as the diluent, the product was exclusively the ethyl compound; and that it is equally susceptible to the action of water is shown by the formation of sodium iodoanilate as a secondary product, when the substance was prepared with sodium, benzyl alcohol, and dry benzene, as we can find no source for this except the atmospheric moisture absorbed through the return condenser during the 2 hours' boiling.

The silver salt of iodoanilic acid is interesting, because it is insoluble in dilute nitric acid, or even in cold, strong nitric acid, which, however, if hot, decomposes it, forming silver iodide.

As with other quinones, phenylhydrazine acted as an excellent reducing agent. In this way we prepared diiododiphenoxyhydroquinone melting with decomposition at 260° (uncor.), tetraiodohydroquinone melting with decomposition at 258° (uncor.), and dibromohydroquinonedimalonic ester melting at 183° (uncor.). From the tetraiodohydroquinone the diacetate was made with acetic anhydride, which begins to decompose at 270°, and melts at 285° (uncor.), a behavior we did not expect from a diaceto compound. The same product was obtained from iodoanil and acetic anhydride, if the action was helped by a few drops of strong sulfuric acid. Such a reaction seems to be a general one for the p-quinones, as acetohydroquinones have been obtained by Sarauw[4] with quinone and acetic anhydride at 260°, or according to Buschka[5] by boiling the two

[1] Jackson, Grindley, *Am. Chem. J.*, **17**, 579 (1895).
[2] Jackson, MacLaurin, *Am. Chem. J*, **38**, 144 (1907); Jackson, Flint, *Ibid.*, **39**, 85; Jackson, P. S. Carleton, *Ibid.*, **39**, 493 (1908).
[3] Jackson, MacLaurin, *Ibid.*, **38**, 157 (1907).
[4] *Ann.*, **209**, 129 (1881).
[5] *Ber.*, **14**, 1327 (1881).

substances with sodium acetate, and by Graebe,[1] when acetyl chloride acted on chloroanil.

When the diiododianilinoquinone was heated with nitrobenzene, the flask was soon filled with vapors of iodine, and the only product we succeeded in isolating from the liquid was a small quantity of dianilinoquinone. We can give no explanation of this curious reaction. If aniline was used instead of nitrobenzene, a considerable yield of dianilinoquinone was obtained, as was to be expected. This reaction had been already observed by Torrey and Hunter,[2] when they caused an excess of aniline to act on diiododiphenoxyquinone.

The diiododiaminoquinone decomposing at 230° (uncor.) was made by the action of alcoholic ammonia on iodoanil. The effect of the quinone oxygen and the iodine on the amino groups is so pronounced that it forms salts with sodium hydroxide but not with dilute acids.

The three dihalogenoquinonedimalonic esters resemble each other closely, all are yellow, and form intensely blue sodium salts soluble in water. Our attempts to saponify them failed, because they are so easily carbonized. Much time was devoted to the study of the decomposition of the sodium salt by cold water, but the amorphous product was so unmanageable that no results worth publishing were obtained. When the dibromoquinonedimalonic ester was treated with bromine and alcohol, a new substance, melting at 172° (uncor.), was formed which can hardly have any formula except $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$, and is therefore dibromoquinonedibromomalonic ester. This view of its constitution was confirmed by the ease with which the second atoms of bromine were replaced by hydrogen, the change being brought about by longer boiling with alcohol and bromine, a reaction we think perhaps analogous to the reduction of iodo compounds by hydriodic acid, and also by aniline, which at the same time seemed to replace the ring bromine atoms by anilino groups. Sodium hydroxide, or similar reagents, gave a reddish brown solution, from which no definite compound was obtained.

An experiment on the action of chloride of iodine on quinone, instead of the expected iodo compound, gave dichloroquinone, a curious result in view of the fact that the chloride of iodine introduces iodine into a great variety of substances, such as, for instance, resorcinol,[3] catechol,[4] phenol,[5] and aniline.[6]

[1] *Ann.*, **146**, 12 (1868).

[2] THIS JOURNAL, **34**, 702 (1912).

[3] Michael, Norton, *Ber.*, **9**, 1752 (1876).

[4] Jackson and Boswell, *Am. Chem. J.*, **35**, 520 (1905).

[5] Schutzenberger, *Jahresb.*, **1865**, 524; Lepetit, *Gazz. chim. ital.*, **20**, 105 (1890)

[6] Stenhouse, *Ann.*, **134**, 213 (1865); Michael and Norton, *Ber.*, **11**, 111 (1878)

Experimental.

The iodoanil was prepared by the method already described.[1] To convert it into diiododiphenoxyquinone 20 g. were treated with the sodium phenolate made by adding 6.2 g. of phenol to 2.6 g. of sodium hydroxide dissolved in 50 cc. of water. After warming for half an hour the product was crystallized once from toluene, which purified it sufficiently for our purposes.

Diiododiphenoxyhydroquinone, $C_6I_2(OC_6H_5)_2(OH)_2$.— Phenylhydrazine was added drop by drop to 2 g. of diiododiphenoxyquinone suspended in hot glacial acetic acid, until no more nitrogen was evolved. The white product was crystallized from benzene or toluene, until it showed the constant melting point 260° (uncor.).

> Subs. 0.2370; AgI, 0.2016.
> Calc. for $C_6I_2(OC_6H_5)_2(OH)_2$: I, 46.51, found I, 45 98.

Properties.— Small, white needles from benzene sintering at 255°, melting fully at 260° (uncor.). It is slightly soluble in cold chloroform, acetone, ether, ethyl acetate, glacial acetic acid, nitrobenzene, or aniline; essentially insoluble in cold carbon tetrachloride, benzene, toluene, or naphtha; freely soluble in any of these solvents if heated. Benzene or toluene is the best solvent for it. Sodium hydroxide gives a colorless solution with it, from which an acid throws down the unaltered substance.

Diiododimethoxyquinone, $C_6I_2(OCH_3)_2O_2$.— Torrey and Hunter's[2] diiododimethoxyquinone dimethylhemiacetal (prepared from diiododiphenoxyquinone and sodium methylate) was warmed a few minutes with a little acetic anhydride. On cooling, bright red needles were deposited, which, after drying on a porous plate, were crystallized from methyl alcohol until they showed the constant melting point 196° (uncor.).

> Subs. 0.2524, 0.1670; AgI, 0 2834, 0 1874
> Calc. for $C_6I_2(OCH_3)_2O_2$: I, 60 47. found. I, 60 68, 60 64

Properties.— It crystallizes in light red needles melting at 196° (uncor.). It is easily soluble in acetone, ethyl acetate, carbon tetrachloride, benzene, or toluene; essentially insoluble in ether, cold alcohol, or water Methyl alcohol is the best solvent for it. Cold water does not attack it, but when hot slowly converts it into iodoanilic acid.

Diiodododiethoxyquinone, $C_6I_2(OC_2H_5)_2O_2$.— This compound was prepared in the same way as the dimethoxy compound. It was crystallized from alcohol till it melted constant at 186° (uncor.).

> Subs. 0.2476, 0.1912; AgI, 0.2602, 0.1998.
> Calc. for $C_6I_2(OC_2H_5)O_2$: I, 56 69; found, I, 56.79, 56.50.

Properties.— It crystallizes in orange red needles melting at 186° (uncor.). Its solubilities are essentially the same as those of the dimethyl

[1] THIS JOURNAL, **36**, 305 (1914).
[2] *Ibid.*, **34**, 702 (1912).

compound. Hot water converts it slowly, sodium hydroxide immediately, into iodoanilic acid.

The diiododiethoxyquinone was also formed in an attempt to make the benzyl derivative by the action of diiododiphenoxyquinone with sodium benzylate made by treating benzyl alcohol dissolved in ether with sodium. The ether had been dried, but not washed before drying, and the small amount of alcohol it contained was enough to convert the whole product into diiododiethoxyquinone, m. 186° (uncor.).

Calc. for $C_6I_2(OC_2H_5)_2O_2$: I, 56.69; found: I, 56.95, 56.40.

Diiododibenzyloxyquinone, $C_6I_2(OC_7H_7)_2O_2$.—Two grams of diiododiphenoxyquinone were treated with the sodium benzylate (made by adding 0.4 g. of sodium to 4 cc. of benzyl alcohol dissolved in 50 cc. of dry benzene; see the preceding paragraph). After heating under a return condenser for 2 hrs. a red solution was obtained mixed with a dark green solid, which we supposed to be principally sodium iodoanilate, because it dissolved in water with the characteristic dark purple color. The residue from the spontaneous evaporation of the benzene solution was freed from benzyl alcohol by washing with a little alcohol, and crystallized from a mixture of benzene and naphtha until it showed the constant m. p. 160° (uncor.).

Subs. 0.1726, 0.2317; AgI, 0.1430, 0.1901.
Calc. for $C_6I_2(OC_7H_7)_2O_2$: I, 44.40; found: I, 44.78, 44.33.

Properties of Diiododibenzyloxyquinone.—It crystallizes in orange-red oblong plates melting at 160° (uncor.). There is no qualitative difference between its solubilities and those of the dimethyl compound. The best solvent for it is naphtha containing a little benzene. Warming with water slowly converts it into iodoanilic acid.

Dibromodibenzyloxyquinone, $C_6Br_2(OC_7H_7)_2O_2$.—Two grams of dibromodiphenoxyquinone were treated with the sodium benzylate (made from 0.4 g. of sodium, 4 cc. of benzyl alcohol and 100 cc. of ether washed till free from alcohol and carefully dried). After heating under a return condenser for an hour the green solid was filtered out. It dissolved in water with the dark purple color characteristic of sodium bromoanilate. The ether was allowed to evaporate spontaneously from the filtrate and the residue, freed from benzyl alcohol by washing with alcohol, was crystallized from naphtha till it showed the constant m. p. 146° (uncor.).

Calc. for $C_6Br_2(OC_7H_7)_2O_2$: Br, 33.44; found: Br, 33.23.

Properties.—It forms orange-red plates, which melt at 146° (uncor.). Its solubilities do not differ qualitatively from those of the corresponding iodo compound, and like that it is saponified slowly by hot water, although unaffected in the cold.

Dibromodiacetoxyquinone, $C_6Br_2(C_2H_3O_2)_2O_2$.—The bromoanilic acid, from which this was prepared, was made by adding to 20 g. of bromoanil 8 g.

of sodium hydroxide dissolved in 125 cc. of water, when, in a short time, the sodium salt separated from the solution, and after dissolving it in the least possible quantity of water, the bromoanilic acid was set free and precipitated by an excess of gaseous hydrochloric acid. Eight grams of the acid were heated with 3 g. of acetic anhydride, until a deep red solution was formed, which, on cooling, deposited yellow crystals. These were washed free of acetic anhydride with dilute alcohol, which, however, saponified a little of the substance, and then crystallized from carbon tetrachloride, till it showed the constant m p 205° (uncor.).

Subs 0.2238, 0 1881, AgBr, 0 2212, 0 1870
Calc for $C_4Br_2(C_2H_4O_2)_2O$, Br, 41 88, found Br, 42 07, 42 31

Properties.—It crystallizes in long, yellow, oblong plates, which melt at 205° (uncor.). It is soluble in alcohol, acetone, ethyl acetate, glacial acetic acid, benzene, or toluene, essentially insoluble in cold ether or naphtha. The best solvent for it is tetrachloride of carbon. It is slowly converted into bromoanilic acid by cold water, quickly by hot water or sodium hydroxide. Its properties, therefore, are analogous in every respect to those of diiododiacetoxyquinone, which has been described in an earlier paper.[1]

Silver Iodoanilate, $C_6I_2(OAg)_2O_2$.—A slight excess of silver nitrate was added to a dilute solution of iodoanilic acid and the red precipitate washed till free from silver nitrate, dried, and warmed with alcohol and benzene when it was dried at 100°. It was analyzed by heating it with fuming nitric acid.

Calc for $C_6I_2(OAg)_2O_2$ Ag, 35 65, found Ag, 35 24

Properties.—It is a dark red amorphous substance insoluble in organic solvents and dilute acids. Even strong nitric acid has no action on it in the cold, but on warming decomposes it with formation of silver iodide.

Diiododiaminoquinone, $C_6I_2(NH_2)_2O_2$.—Two g. of iodoanil were heated with an excess of alcoholic ammonia, and the deep purple product washed first with alcoholic ammonia, later with alcohol, after which it was suspended in a little alcohol, brought into solution with a few drops of sodium hydroxide, and reprecipitated with dilute acid. After this treatment had been repeated several times, it was dried for analysis.

Subs 0 1994, 0 1806, AgI, 0 2400, 0 2198.
Calc for $C_6I_2(NH_2)_2O_2$ I, 65 12, found I, 65 04, 65.79.

Properties.—A brown amorphous solid melting at 230° (uncor.) with evolution of vapors of iodine. It is insoluble in alcohol, acetone, tetrachloride of carbon, glacial acetic acid, benzene, or toluene. A cold solution of sodium hydroxide dissolves it, but it is reprecipitated by dilute acids. When warmed with sodium hydroxide, a small amount of iodoanilic acid is formed.

[1] THIS JOURNAL, 36, 560 (1914)

Diiododianilinoquinone, $C_6I_2(C_6H_5NH)_2O_2$.—Two grams of diiododiphenoxyquinone were heated with a little more than two molecules of aniline and alcohol, until dark purple needles were formed, which were washed with alcohol, and crystallized 3 times from toluene.

Subs. 0.2347; AgI, 0.2042.

Calc. for $C_6I_2(C_6H_5NH)_2O_2$: I, 46.86; found: I, 47.02.

Properties.—Short, dark purple needles, which begin to decompose at 220°, and melt at 240° (uncor.). If heated with aniline, it forms dianilinoquinone, which was recognized by the absence of halogen, and the characteristic carmine solution formed with strong sulfuric acid. When heated with nitrobenzene the diiododianilinoquinone gives off violet vapors of iodine, which fill the upper part of the flask in a short time. A small quantity of dianilinoquinone was isolated from the product, but no other definite compound could be obtained.

Diiododi-p-toluidinoquinone, $C_6I_2(C_7H_7NH)_2O_2$.—This substance was prepared like the preceding and purified by washing with benzene, alcohol and finally with ether.

Calc. for $C_6I_2(C_7H_7NH)_2O_2$: I, 44.55; found: I, 44.87.

Properties.—It appears in dark purple oblong plates with a metallic reflex, which decompose at 205°, turning black and giving off vapors of iodine. Soluble in nitrobenzene; essentially insoluble in alcohol, ether, acetone, chloroform, tetrachloride of carbon, glacial acetic acid, benzene, or toluene.

Diiodoquinonedimalonic Ester, $C_6I_2(CH(COOC_2H_5)_2)_2O_2$.—Two grams of diiododiphenoxyquinone suspended in 15 cc. of absolute alcohol were treated with the sodium malonic ester (made by adding 0.3 g. of sodium to 20 cc. of absolute alcohol, and after the sodium had disappeared, pouring in 4 g. of malonic ester). The greenish black solution, after standing at ordinary temperatures for 12 hrs., had deposited a blue precipitate of the sodium salt, which was washed with alcohol, in which it is not very soluble, and then dissolved in water. Upon adding dilute acid to the blue solution, a yellow precipitate was formed, which was crystallized from 50% alcohol until it showed the constant m. p. 138° (uncor.).

Subs. 0.2377; AgI, 0.1629.

Calc. for $C_6I_2(CH(COOC_2H_5)_2)_2O_2$: I, 37.58; found: I, 37.04.

The same compound, to judge from its color and that of its salt, was formed when iodoanil was treated with sodium malonic ester, but the yield was small, and the purification much more difficult than when the diphenoxy compound was used. In this respect, the iodine compounds resembled the corresponding chlorine compounds.[1]

Properties of Diiodoquinonedimalonic Ester.—It crystallizes from dilute alcohol in yellow fern-shaped forms and melts at 138° (uncor.). It is

[1] Jackson, Grindley, *Am. Chem. J.*, **17,** 579 (1895).

soluble in alcohol, ether, acetone, tetrachloride of carbon, glacial acetic acid, benzene, or toluene. The best solvent for it is 50% alcohol. A dilute solution of sodium hydroxide forms with it a dark blue solution of the sodium salt, which has an intense blue color, and is very soluble in water, very slightly in alcohol, and insoluble in most of the other organic solvents. Attempts to saponify the ester led to no definite result, as it was carbonized by either sulfuric or hydrochloric acid, as soon as the acid was made strong enough to have any action.

Dibromoquinonedimalonic Ester, $C_6Br_2(CH(COOC_2H_5)_2)_2O_2$.—The sodium malonic ester necessary for 2 g. of the dibromodiphenoxyquinone was made by treating 100 cc. of absolute alcohol with 0.3 g. of sodium and then adding 3 g. of malonic ester. The largest yield was obtained by adding the dibromodiphenoxyquinone in small quantities at a time, and shaking vigorously after each addition. The liquid turned bluish green, and, after standing for 6 hrs., the blue precipitate of the salt was washed with alcohol, dissolved in water, and, after filtering out any unaltered diphenoxy compound, precipitated with dilute sulfuric acid. The orange-brown solution thus obtained usually threw down the free substituted malonic ester after a short time, but, if instead a floating tarry mass was obtained, this solidified more slowly on standing. In either case the product was crystallized from 50% alcohol, until it showed the constant m. p. 109° (uncor.).

> Subs 0.3046; AgBr, 0 2003
> Calc. for $C_6Br_2(CH(COOC_2H_5)_2)_2O_2$ Br, 27 49; found. Br, 27 98.

Properties.—It crystallizes in small yellow needles, which melt at 109° (uncor.). It is easily soluble in alcohol, ether, acetone, chloroform, tetrachloride of carbon, carbon disulfide, ethyl acetate, glacial acetic acid, benzene, toluene, or nitrobenzene. With aniline it forms a dark purple solution, with dimethylaniline a deep blue. Dilute hydrochloric acid, or sulfuric acid, forms a dark brown product, which is mostly carbon; dilute nitric acid converts it into a red oil, which does not dissolve; strong nitric acid dissolves it, and dilution throws down an orange-brown tar, from which we could isolate no definite compound; strong sulfuric acid dissolves it with a dark brown color, from which water throws down a black, highly carbonized precipitate. All our attempts to saponify it were baffled by carbonization.

Dilute sodium hydroxide gives a deep blue solution of the sodium salt, which, in a few minutes, takes on a dark reddish purple color. The addition of an acid now precipitates a brown amorphous substance, and the filtrate gives a test for bromide and for alcohol. This reaction seemed to us so interesting that we spent a long time in attempts to determine its nature, but without result.

Dibromohydroquinonedimalonic Ester, $C_6Br_2(CH(COOC_2H_5)_2)_2(OH)_2$.—

Dibromoquinonedimalonic ester dissolved in toluene was treated with a few drops of phenylhydrazine. Nitrogen was given off and the hydroquinone which was deposited was washed with alcohol and crystallized from toluene until it showed the constant m. p. 183° (uncor.).

Calc. for $C_6Br_2(CH(COOC_2H_5)_2)_2(OH)_2$: Br, 27.39; found: Br, 27.05.

Properties.—It crystallizes in short, white prisms, which melt at 183° (uncor.). It is soluble in alcohol, ether, chloroform, benzene, nitrobenzene, or aniline; essentially insoluble in water, naphtha, or glacial acetic acid. Dilute acids have no action on it; saponification with constant boiling hydrobromic acid gave a brown product, from which we could obtain nothing fit for analysis. A dilute solution of sodium hydroxide forms a light green solution, which gradually changes to dark green, then to purple, and finally to a reddish purple. This final solution is probably identical with the one obtained, when the solution of the sodium salt of dibromoquinonedimalonic ester is allowed to stand. The reddish purple solution deposited a white salt, which dissolved in water and gave a white precipitate with an acid. The salt turned bluish green on exposure to the air. It was not studied further.

Dibromoquinonedibromomalonic Ester, $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$.—One gram of dibromoquinonedimalonic ester dissolved in 30 cc. of alcohol was treated with 6 to 8 g. of bromine and the mixture heated for half an hour on the water bath under a return condenser. The yellow needles which formed slowly on cooling, were washed with a little cold alcohol and crystallized from hot alcohol until they showed the constant m. p. 172° (uncor.). They were dried *in vacuo*.

Subs. 0.1796, 0.2636; AgBr, 0.1808, 0.2636.
Calc. for $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$: Br, 43.24; found: Br, 42.84, 42.56.

Properties.—It crystallizes in rosets of small yellow needles, melting at 172° (uncor.), which turn greenish yellow when exposed to the sunlight. It is soluble in acetone, chloroform, ethyl acetate, carbon disulfide, benzene, nitrobenzene, or aniline; very slightly soluble in ether, tetrachloride of carbon, glacial acetic acid, naphtha, toluene, or cold alcohol, soluble in hot alcohol, which is the best solvent for it. Dilute sodium hydroxide gave a reddish brown solution, from which nothing was precipitated on addition of an acid; sodium ethylate, potassium carbonate, or silver oxide gave similar unmanageable results.

When the dibromoquinonedibromomalonic ester was heated with alcohol and bromine for half an hour, yellow needles separated on cooling, which were recognized as dibromoquinonedimalonic ester by the m. p. 108°–109° (uncor.), and the formation of a dark blue solution with sodium hydroxide. The two atoms of bromine in the malonic ester groups may have been replaced by hydrogen by the action of hydrobromic acid, or of the alcohol, or both. If the alcohol causes the reaction, it may explain

the low percentages of bromine found in the analyses, since the compound was crystallized from alcohol.

When a few drops of aniline were added to some dibromoquinonedibromomalonic ester dissolved in alcohol, and the mixture heated for several minutes, a purple substance was deposited, which, after washing with alcohol, melted at 175°–180° (uncor.) with such vigorous decomposition that it swelled to three times its original size. It is slightly soluble in acetone, chloroform, ethyl acetate, carbon disulfide, or benzene; essentially insoluble in alcohol, ether, tetrachloride of carbon, glacial acetic acid, naphtha, toluene, or nitrobenzene. It contains no halogen and dissolves in sodium hydroxide solution, forming a purple liquid, from which an acid liberates the original substance. The two bromine atoms in the malonic ester radicals, therefore, have been replaced by hydrogen, and the compound is probably dianilinoquinonedimalonic ester, but, as it lay outside the immediate field of our work, it was not studied in detail.

Tetraiodohydroquinone, $C_6I_4(OH)_2$.—Two grams of iodoanil suspended in 35 cc. of glacial acetic acid were gently warmed and treated with 3 to 5 drops of phenylhydrazine, nitrogen was given off, and the dark brownish purple color changed to light brown, and the hot acetic acid solution after filtration deposited cream colored crystals. Both these crystals and the light brown residue from the glacial acetic acid grew darker on crystallization from glacial acetic acid, undoubtedly owing to the formation of iodoanil, so that the first crystals were probably the purest specimen we obtained.

Calc. for $C_6I_4(OH)_2$: I, 82.74; found: I, 83.41.

Properties.—It was obtained in its preparation as cream colored crystals, which begin to decompose at 238°, and finally melt at 258° (uncor.). On exposure to the air it quickly turns brown from the formation of iodoanil. This tendency to oxidation is so strong that it could not be purified by crystallization in the air. It is soluble in ether, acetone, chloroform, carbon disulfide, or aniline; nearly insoluble in cold alcohol, ethyl acetate, glacial acetic acid, naphtha, benzene, toluene, or nitrobenzene, but dissolves in each of them, when hot, with the exception of naphtha. It dissolves in a boiling solution of sodium hydroxide, and acidification throws down a white precipitate of the hydroquinone.

p-Diacetoxytetraiodobenzene, $C_6I_4(OC_2H_3O)_2$.—Two grams of the tetraiodohydroquinone were thoroughly moistened with acetic anhydride and heated. In the first 20 minutes little or no action was observed, but after half an hour the substance had gone into solution. By adding a little fused sodium acetate the reaction can be made to take place in a few minutes. The hot solution was poured into water and the acetic anhydride destroyed with acid sodium carbonate, after which the product was crystallized 4 times from benzene and dried at 100°.

Calc. for $C_6I_4(OC_2H_3O)_2$: I, 72.78; found: I, 73.11.

Properties.—It forms small white needles, which begin to decompose about 270° and melt at 285° (uncor.). It is slightly soluble in ethyl acetate; practically insoluble in cold alcohol, ether, acetone, chloroform, tetrachloride of carbon, glacial acetic acid, naphtha, benzene, nitrobenzene, or aniline, but soluble in each of these solvents, when hot, with the exception of alcohol and naphtha. Acids, or alkalies, seem to produce no immediate effect on it.

If iodoanil was heated for 10 or 15 minutes with acetic anhydride, the unaltered substance separated on cooling, but, if a few drops of strong sulfuric acid were added, the same length of heating produced a brown solution, which gave a precipitate with water, that after 4 crystallizations from benzene began to darken at 270° and melted at 284° (uncor.). It was therefore the tetraiodo-*p*-diacetoxybenzene.

Action of Chloride of Iodine on Quinone.—Twenty-five grams of chloride of iodine[1] were passed into 15 g. of quinone suspended in 200 cc. of tetrachloride of carbon, and the mixture gently warmed. After the reaction was complete, the precipitate of iodine was filtered out, the filtrate evaporated to dryness, and after removing the iodine by washing with aqueous potassium iodide the yellow residue crystallized from naphtha, until it showed the constant m. p. 161° (uncor.), which indicated that the substance was dichloroquinone, an inference confirmed by the following analyses:

Subs o 3284, o 2167, AgCl, o 5288, o 3494
Calc for $C_6H_2Cl_2O_2$ Cl, 40 12, found Cl, 39 81, 39 86

CAMBRIDGE, MASS

THE REACTION BETWEEN PHENYL-MAGNESIUM BROMIDE AND UNSATURATED COMPOUNDS THAT CONTAIN A NUMBER OF PHENYL GROUPS.

By DOROTHY A HAHN AND RUBY MURRAY,
Received April 24, 1914

A comparison of the results obtained by treating highly phenylated compounds with the Grignard reagent, shows that phenyl groups, in both α and β positions, to carbonyl, effect a much greater hindrance to the reaction than the same number of groups in the α position. Thus, no reaction can be obtained by boiling tetraphenylpropenone[2]

$$(C_6H_5)_2C = C(C_6H_5)COC_6H_5,$$

with phenylmagnesium bromide, while benzpinacoline,

$$(C_6H_5)_3C.COC_6H_5,$$

[1] Made according to Jackson and Bigelow, *Am. Chem. J.*, 46, 549 (1911).
[2] *Am Chem. J.*, 38, 519 (1907).

reacts fairly readily with the same reagent. A similar resistance has been observed in diphenylpropionyl mesitylene,[1]

$$(C_6H_5)_2CH.CH_2COC_6H_2(CH_3)_3,$$

in which the inactivity of the carbonyl is due to diorthosubstitution.

In order to explain this difference, which is hardly in accord with the ordinary conceptions of steric hindrance, it is necessary to study the reaction with substances that contain other "negative" groups in the place of phenyl.

It is extremely difficult to determine the structure of the products that are obtained by applying the Grignard reagent to such complex substances, but the symmetrical dibenzoylstilbene,

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5,$$

which has benzoyl in place of one of the phenyl groups of tetraphenylpropenone, offered some prospect of success. This was the principal substance used in the following investigation; but, for the sake of comparison, some experiments were made with the simpler dibenzoylcinnamene,

$$C_6H_5COCH = C(C_6H_5)COC_6H_5.$$

We have found that both of these substances react fairly readily with phenyl-magnesium bromide. A benzoyl group, therefore, does not produce an effect equal to that of a phenyl group.

The reaction between dibenzoylcinnamene and phenyl-magnesium bromide gave only two products: dibenzoyldiphenyl ethane and lepidene. Both of these substances are plainly due to 1,4-addition.

$$C_6H_5COCH = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$
$$C_6H_5COCH(C_6H_5)C(C_6H_5) = C(C_6H_5)OMgBr \longrightarrow$$
$$C_6H_5COCH(C_6H_5)C(C_6H_5) = C(C_6H_5)OH.$$
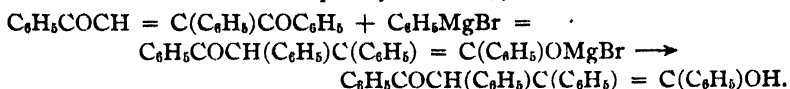
The enolic compound formed, by decomposing the magnesium derivative with water, in part undergoes the usual rearrangement to the corresponding ketone, giving dibenzoyldiphenylethane (I),

$$C_6H_5COCH(C_6H_5)C(C_6H_5)HCOC_6H_5;$$
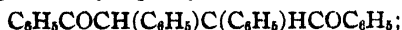
and in part undergoes dehydration, giving lepidene (II) or tetraphenylfurane.

$$C_6H_5COCH(C_6H_5)C(C_6H_5) = COHC_6H_5 \longrightarrow C_6H_5C — CC_6H_5 + H_2O$$
$$(I)$$
$$C_6H_5 C \qquad CC_6H_5$$
$$O \quad (II)$$
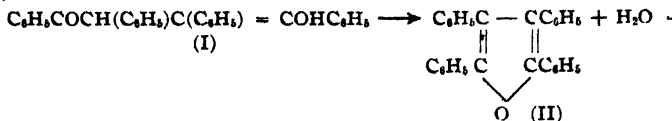
The reaction with dibenzoylstilbene gives two closely related substances of which the structure is somewhat uncertain. The empirical formula of the substances shows that both are formed by the interaction of one molecule of ketone and one molecule of Grignard's reagent. These two

[1] *Am. Chem. J.*, **38**, 519, 555 (1907).

substances give identical products both on reduction and on oxidation. The very close relation existing between them, and the nature of their reduction and oxidation products, indicate that they are due to 1,2-addition of phenyl-magnesium bromide to the carbonyl.

The two reactions possible between dibenzoylstilbene and phenyl-magnesium bromide are represented by the following equations:

I. (1,2-addition):

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$
$$C_6H_5COC(C_6H_5) = C(C_6H_5)C(C_6H_5)_2OMgBr \longrightarrow$$
$$C_6H_5COC(C_6H_5) = C(C_6H_5)COH(C_6H_4)_2$$

II. (1,4-addition):

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$

$$C_6H_5COC(C_6H_5)_2C(C_6H_5) = C\underset{OMgBr}{\overset{C_6H_5}{<}} \longrightarrow C_6H_5COC(C_6H_5)_2C(C_6H_5) =$$

$$C\underset{OH}{\overset{C_6H_5}{<}} \longrightarrow C_6H_5COC(C_6H_5)_2C(C_6H_5)HCOC_6H_5$$
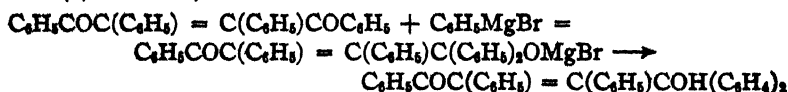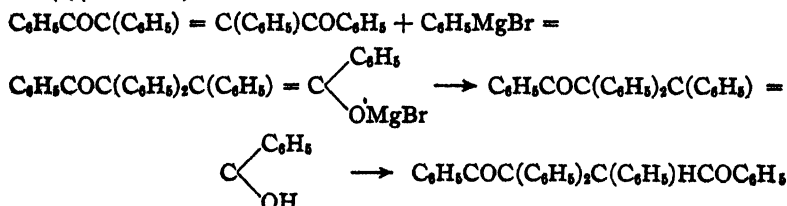
Of these reactions, the first accounts for the existence of two substances of exactly the same chemical properties, by offering the possibility of geometrical isomerism. The two substances obtained by this reaction cannot represent 1,2- and 1,4-addition, respectively, since it is impossible for substances of the formula

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5$$

and

$$C_6H_5COC(C_6H_5)_2CHC_6H_5COC_6H_5,$$
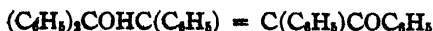
to give the same reduction product by addition of two hydrogen atoms and subsequent loss of water.

The two substances formed by the action of dibenzoylstilbene and phenyl-magnesium bromide melt at 208° and 157°, respectively. Both substances, on reduction, give a product melting at 185°. The analysis and molecular-weight determinations of this substance show that there has been no loss of phenyl groups during reduction. Assuming that the substances melting at 208° and 157° are geometrical isomers, and the result of 1,2-addition of phenyl-magnesium bromide to dibenzoylstilbene, the formation of their common reduction product may be represented by the following equations.

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5 + H_2 =$$
$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)CHOHOC_6H_5 \longrightarrow$$
$$(C_6H_5)_2C.C(C_6H_5) = C(C_6H_5)CH.C_6H_5 + H_2O$$
$$\underline{\qquad\qquad O \qquad\qquad}$$
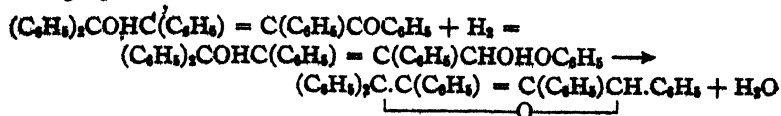
And if these equations correctly express the course of the reaction, it should be possible to open the ring by applying Grignard's reagent. It was found that the reduction product melting at 185° reacted readily with phenyl-magnesium bromide. The addition product was decomposed with ice and hydrochloric acid, and a crystalline substance melting at 232° was separated. Analysis showed it to be less rich in oxygen than the substance from which it was obtained. Its composition may be accounted for by supposing that the opening of the ring was attended by a loss of one molecule of water from two molecules of condensation product:
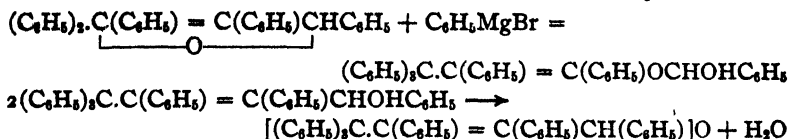
$$(C_6H_5)_2.C(C_6H_5) = C(C_6H_5)CHC_6H_5 + C_6H_5MgBr =$$
$$\underset{\underline{\quad\quad O \quad\quad}}{}$$

$$(C_6H_5)_2C.C(C_6H_5) = C(C_6H_5)OCHOHC_6H_5$$
$$2(C_6H_5)_2C.C(C_6H_5) = C(C_6H_5)CHOHC_6H_5 \longrightarrow$$
$$[(C_6H_5)_2C.C(C_6H_5) = C(C_6H_5)CH(C_6H_5)]O + H_2O$$

The two substances formed by the action of phenyl-magnesium bromide and dibenzoylstilbene give identical products when oxidized with chromic oxide dissolved in acetic acid. The process of oxidation does not always take the same course however, and it was found difficult to arrange the conditions so as to control it. In a series of experiments, the oxidation products showed that the original molecule had sometimes been completely broken down, and sometimes only partially broken down during oxidation. When the decomposition was complete the products were benzoic acid, benzil and benzophenone. Small quantities of a fourth substance were accumulated as the result of a series of oxidations. This substance melts at 143° and represents the incomplete breaking down of the original molecule by oxidation. Its constitution was arrived at by analysis and molecular-weight determinations and by a study of its reduction product. The substance was readily reduced, and its reduction product, melting at 135°, was identified as triphenylvinyl alcohol. The process of oxidation leading to the formation of the substance melting at 143° may be represented by the equations:

$$(C_6H_5)_2COH.C(C_6H_5) = C(C_6H_5)COC_6H_5 + O =$$
$$(C_6H_5)_2COH.C(C_6H_5)C(C_6H_5)COC_6H_5$$
$$\underset{\underline{\quad O \quad}}{}$$

$$(C_6H_5)_2COH.C(C_6H_5).C.(C_6H_5)COC_6H_5 + H_2O + O =$$
$$\underset{\underline{\quad O \quad}}{}$$
$$(C_6H_5)_2COHC(C_6H_5)COHC_6H_5 + C_6H_5COOH$$
$$\underset{\underline{\quad O \quad}}{}$$
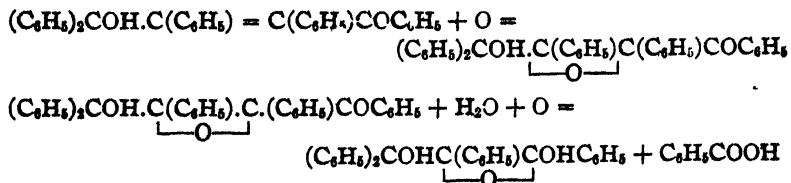
The reduction of this substance to triphenylvinyl alcohol may be represented by the equation:

$$(C_6H_5)_2COHC(C_6H_5)COHC_6H_5 + 2H_2 =$$
$$\underset{\underline{\quad O \quad}}{}$$
$$(C_6H_5)_2CHCOC_6H_5 + C_6H_5CHO + 2H_2O$$
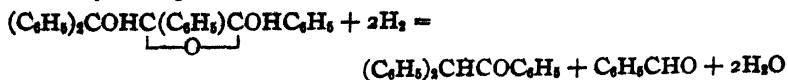
Further confirmation of the assumption that the substances melting at 208° and 157° are geometrical isomers of the formula

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5,$$
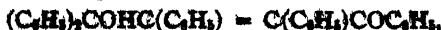
is to be found in their behavior toward acetic anhydride. When pure 208° or pure 157° is dissolved in acetic anhydride, an equilibrium mixture is obtained from which both substances crystallize.

In conclusion, it will be seen, by comparing the reactions of dibenzoyl-cinnamene and dibenzoylstilbene with phenylmagnesium bromide, that the introduction of a phenyl group in the β position to carbonyl, offers resistance to 1,4-addition. Thus, $C_6H_5COCH = C(C_6H_5)COC_6H_5$ shows 1,4-addition of phenylmagnesium bromide and

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5,$$

does not. This is in agreement with results obtained by Kohler,[1] where α,β-triphenylpropenone, $C_6H_5CH = C(C_6H_5)COC_6H_5$, gave a yield of 100% of a 1,4-addition product when treated with phenylmagnesium bromide, and tetraphenylpropenone, $(C_6H_5)_2C = C(C_6H_5)COC_6H_5$, gave no reaction when boiled with the same reagent.

The reactivity of the carbonyl in dibenzoylstilbene,

$$C_6H_5COC = C.COC_6H_5$$
$$\quad\quad | \quad\quad |$$
$$\quad C_6H_5 \quad C_6H_5$$
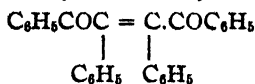
as compared with its complete inactivity in tetraphenylpropenone,

$$(C_6H_5)_2C = C.COC_6H_5$$
$$\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad C_6H_5$$
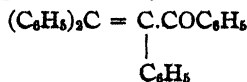
is curious. It would seem as if the reactivity of the carbonyl group with phenylmagnesium bromide were more dependent upon other factors than upon the presence of a phenyl group in the α position.

Experimental.

The condensation of dibenzoylcinnamene with phenyl-magnesium bromine took place readily. The dibenzoylcinnamene was prepared as described by Jopp, Klingemann[2] and was added in finely powdered form to an ethereal solution of the magnesium compound. Fifteen parts by weight of ketone were used for every five parts of magnesium and every thirty-five parts of phenyl bromide. The ketone was added slowly, with constant shaking, and in small portions, which were allowed to dissolve completely before new portions were added. When all of the ketone had been added, the magnesium compound was decomposed at once by shaking with ice and hydrochloric acid, and the ethereal solution was then washed and dried over calcium chloride. The ethereal solution, on

[1] *Am. Chem J.*, **38**, 515 (1907)
[2] *Trans Chem. Soc*, **57**, 673

evaporation, yielded a mixture of products which were separated by fractional crystallization from acetone. The mixture was found to consist of four substances, two of these representing the primary addition products of the reaction between dibenzoylcinnamene and phenylmagnesium bromide, and two representing secondary products resulting from the oxidation of the primary products.

Various modifications of this method of procedure were tried in attempts to minimize the amounts of secondary products. Glacial acetic acid was added at once to the dry ethereal solution, and most of the ether evaporated. The acetic acid, on cooling, precipitated a white crystalline mass, which, when filtered, dried, and weighed, was found to represent about 90% of solid product. The precipitate, however, consisted of a mixture which it was again necessary to separate by fractional crystallization. The only advantage of this method was that the separation of the mixture was in this case quicker and more complete.

In the separation of the mixtures obtained as the result of this condensation, the best method of procedure was to digest first with chloroform. Repeated extractions with small quantities of chloroform left a white insoluble residue which melted quite sharply and was found to be an almost pure substance. On crystallization from benzene this substance melted at 256°. The addition of a very small quantity of ether to the solution of substances in chloroform caused the separation of a second substance in almost pure state. The white crystalline precipitate was filtered and washed with ether, and, after crystallization from acetic acid, melted at 212–213°. The filtrate was then concentrated and hot alcohol was added. On cooling, glistening plates separated. These, after crystallization from acetic acid, melted at 175° and represented from 40-60% of the product of the condensation. A fourth substance was separated by concentrating the mother liquors. It was much more soluble than the other substances and was present in the mixtures only in very small quantities. After recrystallization from alcohol it melted at 157°.

An average yield of about 50% of the product melting at 175° was obtained directly and in almost pure condition, by adding glacial acetic acid to the magnesium addition product obtained in the reaction between dibenzoylcinnamene and phenylmagnesium bromide. The acid was added quite slowly to the ethereal solution of the magnesium compound, and the heat of the reaction was utilized to partially evaporate the ether. A substance separated on cooling which, after two recrystallizations from acetic acid, melted at 175°.

The substances melting at 175° and 256° were analyzed and were found to be lepidene and dibenzoyldiphenylethane, respectively. The identity of the lepidene was established by a study of its relationships and transformations, and by comparison with a specimen obtained by heating

benzoin and hydrochloric acid saturated at 8°, in a sealed tube at 140°.[1] The identity of dibenzoyldiphenylethane was established by analysis, by comparison with a specimen obtained by the reduction of hydroxy lepidene with acetic acid and zinc, and by its behavior toward concentrated sulfuric and concentrated hydrochloric acids. The substance dissolved in concentrated sulfuric acid to give a green solution which gradually changed to brown. The solution, when decomposed with water and extracted with ether, gave lepidene.[2] These two substances represent the primary products of the reaction between dibenzoylcinnamene and phenylmagnesium bromide.

The substances melting at 212° and 157° were found to be dibenzoylstilbene and dihydroxylepidene, respectively. Their identity was established by comparison with specimens prepared by the oxidation of pure lepidene—with nitric acid[3] and by the oxidation of hydroxylepidene—with chromic oxide in acetic acid.[4] The condensation reaction between the first of these substances and phenyl magnesium bromide forms the main portion of the present paper.

Dibenzoylstilbene was prepared in quantity by oxidizing pure lepidene, dissolved in acetic acid, with a mixture of nitric and acetic acids or with a solution of chromic oxide in acetic acid. Since the separation, of pure lepidene was a somewhat tedious process, and since dibenzoyl stilbene was obtained along with lepidene as a result of the reaction between dibenzoylcinnamene and phenylmagnesium bromide, the attempt was made to prepare dibenzoylstilbene directly from the condensation product without separating the lepidene. In general, two methods of procedure were followed: In the first case the dry ethereal solution, containing lepidene, dibenzoyldiphenylethane, and hydroxylepidene, was treated with a mixture of nitric acid and acetic acid. During the oxidation the greater part of the ether was evaporated, and on cooling, quite pure hydroxylepidene separated. The yield varied from 40-60% of theoretical, but the melting point of the product remained at 205-206°, even after repeated crystallizations and although analysis for carbon and hydrogen showed the substance to be pure Rather better results were obtained in the second case, where the oxidation was effected by means of bromine. This was added directly to the ethereal solution of the magnesium addition product formed by the action of dibenzoylcinnamene and phenylmagnesium bromide. One molecule of bromine was calculated for every molecule of dibenzoylcinnamene. A slight excess of the calculated quantity of bromine was always used; but it was found, as the re-

[1] Z. Chem., 1867, 313.
[2] Ber., 22, 855 (1889).
[3] Z. Chem , 1867, 314
[4] Z. Ibid., 1871, 483.

sult, of a series of experiments, that any considerable excess of bromine was harmful to the reaction, since it led to the formation of secondary products which interfered with the separation of hydroxylepidene. In one case, where a large quantity of bromine was used, a yield of 60% of dibromolepidene was obtained.

A convenient method of procedure was as follows: The bromine was added slowly and with constant shaking, and the temperature was not allowed to rise. After it had been added the mixture was decomposed at once by shaking with ice and hydrochloric acid, when an immediate separation of dibenzoylstilbene took place. The thick oily ethereal soluture was decanted and washed. After it had been separated from water as completely as possible, the mass was filtered under pressure, the process of filtration being facilitated by the addition of small quantities of cold acetic acid to the oily mass. The precipitate was finally washed repeatedly with small quantities of acetic acid. The substance, after one crystallization from acetic acid, melted at 212°–213°, and the results of analysis for carbon and hydrogen showed it to be pure dibenzoylstilbene. The yield was 60–80% of theoretical, and this method was the one finally employed for the preparation of the dibenzoylstilbene used in the following experiments:

The reaction between dibenzoylstilbene and phenylmagnesium bromide took place readily in the cold. The hydroxylepidene used in the condensations was prepared by all of the four methods described, and the results of the reactions were found to be the same in the case of all specimens. The method of procedure was as follows: 15 g. of finely powdered dibenzoylstilbene were added slowly to an ethereal solution containing 5 g. of magnesium and 35 g. of phenyl bromide. After the addition of the ketone the mixture was decomposed at once by shaking with ice and hydrochloric acid. The ethereal solution was separated, washed, and dried over calcium chloride. Usually the separation of a white crystalline solid took place at once, but sometimes the separation of the substance was very slow and very incomplete. The substance was filtered and washed with ether, and, after several recrystallizations from glacial acetic acid, melted at 208°. In a series of about twenty experiments the yield varied from 75–85° of pure product. From the ethereal filtrate from this substance a second product crystallized. This was much more soluble than the first and its separation was much slower. It was purified by repeated crystallizations from acetone, from which it separated in large rhombic crystals melting at 157°. These two substances represent the sole products of the reaction between dibenzoylstilbene and phenylmagnesium bromide.

An attempt was made to facilitate the separation of the substance melting at 208° by adding acetic acid to the dry ethereal solution obtained as a result of the condensation. In the process the ether was distilled off

and the temperature was allowed to rise to 100°. It was hoped that on cooling most of the substance melting at 208° would separate out from the solution. Crystals began to separate from the mixture almost immediately, but the separation was very slow and was complete only after several days. The crystalline product was filtered and washed with acetic acid. It was found to consist of an almost pure substance, which after several crystallizations, melted at 157°, and was identical with the substance mentioned in the preceding experiment. In a series of experiments, the yield of pure substance melting at 157° varied from 70–90%. The mother liquids yielded small quantities of the substance melting at 208°, and all of the material used in the successive condensations was quantitatively accounted for.

In order to ascertain whether the substance melting at 208° was unstable in the presence of acid, 20 g. of pure substance were added to 200 cc. alcohol, and the alcohol was then saturated with dry hydrogen chloride gas. Although the substance melting at 208° is almost insoluble in alcohol, it slowly dissolved in the alcoholic solution of hydrogen chloride, the dry gas being passed into the mixture until the solution of the substance melting at 208° was complete. The separation of a crystalline solid from the alcoholic solution began immediately on cooling, but the crystals formed slowly and the process was complete only after several days. The crystalline precipitate was filtered and washed and was found to consist of an almost pure substance. After recrystallizing several times from ether, and then from chloroform-alcohol mixtures, this substance melted at 157°. The yield varied from 80 to 90%. The mother liquors slowly yielded the substances melting at 157° and 208° and all of the material was finally accounted for quantitatively. By modifying the experiment, and by adding a small quantity of alcohol to the dry ethereal solution obtained by condensing dibenzoylstilbene and phenylmagnesium bromide, and then saturating the mixture with dry hydrogen chloride, it was found possible to obtain directly yields of from 80 to 90% of the substance melting at 157°.

Thus it was found possible in the condensation of dibenzoylstilbene and phenylmagnesium bromide, so to modify the procedure as to obtain an average yield of 80% of either of the two products of this reaction. A study of the transformations of these two substances showed that they were very closely related.

γ-Benzoyltetraphenylpropenol, $C_6H_5CO.C(C_6H_5) = C(C_6H_5)COH(C_6H_5)_2$. —This substance, melting at 208°, was one of the products resulting from the reaction between dibenzoylstilbene and phenylmagnesium bromide. The substance separated from the ethereal solution in almost pure condition. It was purified by several rapid recrystallizations from glacial acetic acid

0.1073 g. and 0.1167 g. of subs. gave 0.3443 and 0 3737 g. CO_2 and 0.0536 and 0.0584 g. H_2O.

Calc. for $C_{34}H_{26}O_2$. C, 87.55; H, 5.58, found: 87.51 and 87 32, 5 55 and 5 54

γ-Benzoyltetraphenylpropenol is difficultly soluble in ether, almost insoluble in alcohol, soluble in hot acetic acid and difficultly soluble in cold acetic acid; soluble in acetone and very soluble in chloroform. When left in contact with alcohol for a long time it slowly dissolves. In solution in acetic acid and acetic anhydride it is slowly changed into a substance having the same empirical formula and melting at 157°. When crystallized from acetone or from chloroform-alcohol mixtures it slowly took up water and passed over into a hydrate. This process was slow and was complete only after a great number of recrystallizations from these solvents. It was followed by repeated analyses of the substance during the process of recrystallization. It was found that the percentage of carbon in the substance decreased until a limit was reached, corresponding to the addition of one molecule of water to one molecule of substance. At intermediate stages mixtures of the hydrate and of the anhydrous substance crystallized out together.

0.1769 and 0.1825 g subs gave 0 5491 and 0 5661 g CO_2, and 0 0950 and 0 0984 g. H_2O

Calc for $C_{34}H_{26}O_2$ H_2O C, 84 3, H, 5 8, found 84 6, 84 5 and 6 0, 5 9

The hydrate crystallized from acetone in very large transparent plates or prisms that melted at 203-206°. Its solubility and appearance was the same as that of the anhydrous form. It was, however, very unstable and lost water at ordinary temperatures, the clear transparent crystal becoming opaque and coated with a white powder. When heated at 130° it rapidly lost in weight, but the loss in weight never corresponded to the loss of one molecule of water. In the hope of obtaining quantitative results showing the loss of one molecule of water the hydrate was dissolved in acetic anhydride. The substance separated from this solvent on cooling and was recrystallized once from the same solvent and analyzed.

0 1462 g subs gave 0 4658 g. CO_2 and 0 0708 g. H_2O
Calc for $C_{34}H_{26}O_2$ C, 87 55, H, 5 58, found 86 88 and 5 38

It was observed that the melting point of the product crystallizing from acetic anhydride had been lowered to 190–192°. This was interpreted as due to the formation of a small quantity of the low melting isomer; and such was probably the case, since, after extracting several times with small quantities of anhydrous ether and recrystallizing from glacial acetic acid, the melting point of the product was raised to 204–206° and the percentage of carbon and hydrogen remained unchanged.

The molecular weight of the anhydrous form of γ-benzoyltetraphenyl-propenol was determined by the freezing-point method. Solvent benzene:

Calc. for $C_{54}H_{40}O$: M, 466; found: 425, 419, 428, 410.

γ-*Benzoyltetraphenylpropenol*, $C_6H_5COC(C_6H_5) = C(C_6H_5)COH(C_6H_5)_2$, melting at 157°, was formed together with its geometrical isomer when dibenzoylstilbene reacted with phenylmagnesium bromide. It may be prepared by starting with the pure substance melting at 208° and dissolving it in alcohol that has been saturated with hydrogen chloride gas. The substance was purified by crystallization, first from ether and then from acetone.

0.2021 and 0.1598 g. subs. gave 0.6490 and 0.5124 g. CO_2 and 0.1086 and 0.0852 g. H_2O.

Calc. for $C_{54}H_{40}O_3$: C, 87.55; H, 5.58; found: 87.5, 87 4 and 5.9, 5.9.

Molecular-weight determination by the freezing-point method. Solvent benzene, $K = 5000$.

Calc. for $C_{54}H_{40}O$: M, 466; found: 447, 448, 440.

Molecular-weight determination by the boiling-point method. Solvent benzene, $K = 2160$.

Calc. for $C_{54}H_{40}O_7$: M, 466; found: 378, 433, 433.

The substance melting at 157° was readily soluble in ether, acetic acid, hot alcohol and acetone. It easily separated from the isomeric form melting at 208° by extraction with ether, and then recrystallized from acetone or from chloroform-alcohol mixtures. It separated from acetone in the form of large plates or prisms, resembling very closely the crystalline form of its geometrical isomer.

When boiled with acetic anhydride the substance melting at 157° was slowly changed into the high melting form. Eleven grams of substance were boiled with acetic anhydride in a flask connected with a return condenser for 24 hours. After evaporating off most of the anhydride a mixture was obtained from which 0.35 g. of pure 203–206° was finally separated.

Reduction of γ-*Benzoyltetraphenylpropenol*.—The substances melting at 208° and 157° were attacked by reducing agents. With stannous chloride and hydrochloric acid, and with hydrogen iodide and red phosphorus, each gave a reduction product melting at 185°.

Pentaphenylbutenyl Oxide, $(C_6H_5)_2CC(C_6H_5) = C(C_6H_5)CHC_6H_5$.—In

general, the same method of procedure was followed in the reduction of γ-benzoyltetraphenylpropenol; but the high melting form was much less reactive than the low melting form, and the time required for any given reaction was therefore greater. In reducing with stannous chloride, the substance was dissolved in alcohol or in a mixture of chloroform and alcohol, the calculated quantities of stannous chloride and hydrochloric acid added, and the mixture heated on a water bath for several days. When the high melting form was used, it was necessary to heat the mixture for ten days or more in order to insure a complete reaction. During

the heating, fresh quantities of hydrochloric acid were added at intervals. At the close of the reaction the mixture was poured into water and the oil extracted with ether. On evaporation of the ether, a substance crystallized out which, after several recrystallizations from alcohol, melted at 185°. The reaction was never quantitative, 5 g. of substance yielding 0.5 g. of this reduction product; and, in the case of both the high and the low melting forms, the greater part of the original substance used for the reaction was recovered unchanged. In reducing with hydrogen iodide the usual procedure was followed. The substance was heated with hydrogen iodide and red phosphorus in a sealed tube at 160° for 24 hrs., and at the end of that time the contents of the tube were extracted with ether, and the ether washed and dried. On evaporation of the ether, a substance crystallized out, and, after recrystallization from alcohol, melted sharply at 185°. Two specimens of this reduction product prepared respectively, from the high melting and the low melting forms of γ-benzoyltetraphenylpropenol were analyzed after their identity had been established.

0.1631 g. subs. (from 208°) gave 0.5395 g. CO_2 and 0.0844 g. H_2O.
0.1503 g. subs. (from 157°) gave 0.4962 g. CO_2 and 0.0788 g. H_2O.
Calc. for $C_{34}H_{26}O$: C, 90.6; H, 5.7; found: 90.2, 90.0 and 5.7, 5.8.
The molecular weight was determined (a) by the boiling-point method. Solvent chloroform, K = 3590
Calc. for $C_{34}H_{26}O$: M, 450; found: 534, 506, 491, 480, 493, 494.
(b) By the freezing-point method, solvent benzene, K = 4900.
Calc. for $C_{34}H_{26}O$: M, 450; found: 502, 430, 421.

Pentabutenyl oxide is difficultly soluble in cold alcohol and ether and readily soluble in chloroform and in hot alcohol. It crystallizes from hot alcohol in the form of large plates that grow in characteristic rosetlike groups. The substance reacts with phenylmagnesium bromide to give a crystalline addition product.

Hexaphenylbutenyl Ether [$(C_6H_5)_3CC(C_6H_5)$ = $C(C_6H_5)CH(C_6H_5)$]O, was prepared by adding pentaphenylbutenyl oxide, in the form of a fine powder, to an ethereal solution of phenylmagnesium bromide. There was no apparent reaction in the cold, but solution took place quickly after the mixture had been warmed for a moment on the water bath. The magnesium addition product was decomposed at once by shaking with ice and hydrochloric acid. The separation of a white crystalline solid took place immediately. It was filtered and crystallized several times from chloroform-alcohol mixtures from which it separated in the form of large transparent plates or prisms melting at 232°.

0.1389 and 0.1063 g. subs. gave 0.4719 and 0.3603 g. CO_2 and 0.0737 and 0.0566 g. H_2O.
Calc. for $C_{46}H_{34}O$: C, 92.4; H, 5.9; found: 92.6, 92.4 and 5.9, 5.9.

Oxidation of γ-Benzoyltetraphenylpropenol.—Both substances formed by the action of phenylmagnesium bromide and dibenzoylstilbene gave the

products when oxidized with chromic oxide in acetic acid. The low melting form was very readily oxidized and reduced chromic oxide as rapidly as it was added, while the high melting form was reduced very slowly and its oxidation was complete only after prolonged heating. The method of procedure in the case of the substance melting at 157° was to dissolve the substance in acetic acid and to add to its hot solution a solution of chromic oxide in the same solvent. The reagent was added rapidly with constant shaking, until a permanent brown color remained for a moment or two. The solution was then poured immediately upon ice, when a solid precipitate usually separated. This was filtered and the filtrate was repeatedly extracted with ether. The ethereal solution was extracted several times with a solution of sodium carbonate to remove acids, washed, and dried over calcium chloride. The aqueous solution containing sodium carbonate gave a heavy white precipitate when acidified with hydrochloric acid, and the precipitate, after several crystallizations, was identified as benzoic acid. The ethereal solution, on evaporation, yielded a mixture of three substances, two of which were identified as benzil and benzophenone, while the third was found to be a new substance. The precipitate which separated when the oxidizing mixture was poured upon ice, consisted almost entirely of this third substance, and it was most easily isolated at this point. The quantities of this substance obtained in successive experiments varied greatly—10 g. portions of the substance melting at 157° yielding from a few tenths of a gram to as much as 3 g. We were not able to determine the conditions most favorable for the formation of this substance, but the rapidity with which the oxidation was carried through seemed to be a determining factor. The substance, after several crystallizations from alcohol, melted sharply at 143°.

In the case of the high melting form of γ-benzoyltetraphenylpropenol, the method of procedure was the same except that the chromic oxide was reduced so slowly that it was impossible to follow the course of the reaction by the change in color. Even after boiling with chromic oxide for fifteen minutes, the greater part of the original substance was recovered unchanged. The unchanged portion of the substance melting at 208° was, because of its insolubility in most solvents, readily separated from the oxidation products. These were found, as in the case of the substance melting at 157°, to consist of benzoic acid, benzil, benzophenone and a third, neutral substance melting at 143°. This last substance was isolated only in very small quantities from the oxidation products of the high melting isomer, and was found only when oxidation was incomplete and where part of the original substance was recovered unchanged. The oxidation of the isomer melting at 208° was complete after boiling the substance for several hours with chromic oxide in solution in acetic acid,

but the only products of oxidation in this case were benzoic acid, benzil and benzophenone.

As shown in the introduction, the product (m. p. 143°) obtained by oxidizing both the high and low melting forms of γ-benzoyltetraphenyl-propenol has the formula represented by

$$(C_6H_5)COHC(C_6H_5)COHC_6H_5.$$
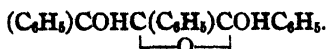
It was purified by several crystallizations from hot alcohol, from which it separated in well-defined plates having the characteristic habit of growing in roset-like groups.

0.1620 and 0.1088 g. subs. gave 0.4875 and 0.3264 g. CO_2 and 0.0763 and 0.0468 g. H_2O.

Calc. for $C_{27}H_{22}O_2$: C, 82.2; H, 5.5; found: 81.9, 81.8 and 5.2, 5.2.

The molecular weight was determined (a) by the boiling-point method, solvent chloroform, K = 3590.

Calc. for $C_{27}H_{22}O_2$: M, 394; found: 369, 372, 365, 365, 362, 366.

(b) by the freezing-point method, solvent benzene, K = 4900.

Calc. for $C_{27}H_{22}O_2$: M, 394; found: 334, 326, 363, 362, 366, 365

The substance is quite soluble in all organic solvents. It dissolved in concentrated nitric acid and concentrated sulfuric acids to give a brilliant red solution. Oxidized in acetic acid with chromic oxide, it gave benzophenone and benzoic acid.

The substance was not acted upon by metallic sodium and alcohol, but when dissolved in acetic acid it was slowly acted upon by zinc and hydrochloric acid. The product of the reaction was a substance melting at 135°. The same reduction product was obtained when the substance in solution in alcohol was reduced by the action of stannous chloride and hydrochloric acid. The method of procedure in this case was to dissolve the substance in alcohol, add the calculated stannous chloride and hydrochloric acid, and heat on the water bath for 6 hrs. A crystalline product separated on cooling and this was filtered. The addition of water to the filtrate caused more of this substance to crystallize and this was again filtered. The filtrate had a strong odor of benzaldehyde. The reduction product, separating in this way, was found to be almost pure, and after one or two crystallizations from alcohol melted sharply at 135°. The analysis and molecular-weight determinations of this substance showed that it corresponded to the formula $C_{20}H_{16}O$; and it was identified as triphenylvinyl alcohol by comparison with a specimen of that substance prepared by heating trichloroacetyl chloride with benzene in the presence of aluminium chloride.

MT. HOLYOKE COLLEGE LABORATORY,
BRYN MAWR COLLEGE LABORATORY.

4-BROMO-6-NITRO-m-CRESOL AND SOME OF ITS DERIVATIVES.

BY L. CHAS. RAIFORD AND GLADYS LEAVELL.
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In 1889 Claus and Hirsch[1] studied the behavior of m-cresol toward bromine and other reagents. Among the derivatives reported was a dibromo compound obtained by brominating 6-nitro-m-cresol,[2] which they named 2,4-dibromo-6-nitro-m-cresol, and to which they assigned the structure,
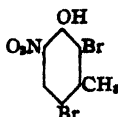
The analysis reported for bromine agreed with the formula given, but, beyond this, no details as to the method of preparation, properties, direct proof of structure of this compound or any of its derivatives are recorded. The melting point was given as 93°.[3]

In a study of chloroimidoquinones[4] one of the authors, working with Stieglitz, had occasion to nitrate 2,4,6-tribromo-m-cresol[5] by a modification of Zincke's[6] method, and found that the reaction gave a pair of mononitrodibromo-m-cresols that melted at 87° and 134°, respectively. These compounds were identified by the preparation and study of several of their derivatives, and their structures were decisively proved. The structure of the compound melting at 87° was established by preparing it from 2,4,6-tribromo-m-cresol, in which the positions of the bromine atoms are known, and by determining the relative positions of the hydroxyl and nitro groups in the substance itself. Through the preparation and reduction[7] of the nitrocarbonate, and the subsequent rearrangement of this reduction product to the corresponding urethane, these positions were found to be adjacent (ortho). Additional evidence tending to support the view that these groups are adjacent is found in the fact, recently observed, that the

[1] J. prakt. Chem., [2] 39, 62 (1889)

[2] Ann. Chem. (Liebig), 52, 217 (1883), and 259, 210 (1890).

[3] It will be shown below that a dibromonitrocresol, probably identical with Claus and Hirsch's product, is formed under the same conditions and along with the monobromo compound mentioned in the title of this paper; though the most careful purification possible failed to raise the melting point above 87°. The dibromo compound here obtained was found to be identical with a substance (Am. Chem. J., 46, 427 (1911)) the structure of which was shown by one of us to be 2,4-dibromo-6-nitro-m-cresol.

[4] Am. Chem J., 46, 417 (1911)

[5] Bull. soc. chim., 46, 275 (1886).

[6] J. prakt. Chem., [2] 61, 56 (1900).

[7] Am. Chem J., 23, 14 (1900).

amine obtained by the reduction of the nitro compound may, under suitable precautions, react with nitrous acid to give a diazoxide.[1] Taken together, these facts show the compound to be 2,4-dibromo-6-nitro-m-cresol, with the structure suggested by Claus and Hirsch[2] for their product.

While the above-mentioned work on chloroimidoquinones was being done, an attempt was made to repeat Claus and Hirsch's experiment[3] with the hope of proving the identity of the compound melting at 87° with that reported to melt at 93°. It was noted that two products were formed but lack of time prevented further investigation then. It has now been found that, when 6-nitro-m-cresol is brominated in glacial acetic acid solution, starting the reaction at the room temperature, a monobromo product is formed to the extent of about 60% of that theoretically possible. After removal of this substance, which crystallizes rapidly from the reaction mixture after all bromine has been added, pouring the filtrate into water gives an additional product, the 2,4-dibromo-6-nitro-m-cresol, m. p. 87°, mentioned above. In this paper we have reported the results of our investigation of the monobromo compound, including some of its derivatives and the determination of its structure.

In order to determine the position of bromine in this compound, the purified product was subjected to the further action of bromine. A substance was obtained which, after crystallization from alcohol, melted at 87°. A mixture of this and 2,4-dibromo-6-nitro-m-cresol melted at the same temperature, which indicated that the products were identical, and that the monobromo compound must have formula (I) or (II) as given below:
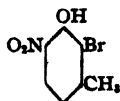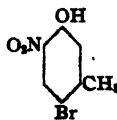
The proof that in this compound bromine occupies position (II) or (IV) was further confirmed as follows: The monobromo compound, melting at 126°, was nitrated at a temperature (30–35°) slightly above that of the room, and gave a monobromodinitro compound, melting at 77°, which was characterized by the study of several of its derivatives (see experimental part). When the last named substance was nitrated at a higher

[1] Meldola, Woolcott and Wray (J. Chem. Soc., 69, 1332 (1896)) state that the formation of a diazo-oxide (or quinonediazide, Wolff, Ann. Chem. (Liebig), 312, 126 (1900)) is proof of the ortho relationships of the nitro and hydroxyl groups. The literature, however, mentions cases where compounds having apparently the characteristics of diazo-oxides have been prepared from p-aminophenols.

[2] Loc. cit.

[3] They give no details as to methods.

temperature, bromine was replaced, and 2,4,6-trinitro-*m*-cresol[1] was obtained.

In order to gain further insight as to which of the two positions was occupied by bromine, it was proposed to study the ethyl ether of the compound in question. In their work on the derivatives of *o*- and *p*-nitro-*m*-cresol, Staedel and Kolb[2] found that 6-nitro-*m*-cresol was easily converted into its ethyl ether, and that when the latter was nitrated the second nitro group took a position para to the ethoxy group. The relative positions of these groups were determined by showing that the dinitro ether mentioned above is identical with that one obtained in a similar way from 4-nitro-*m*-cresol. These experiments were repeated by us, and Staedel and Kolb's conclusions confirmed, with a view to making use of them in determining the position of bromine in our compound. The reactions may be indicated as follows:

| (I) | (II) | (III) | (IV) | (V) |
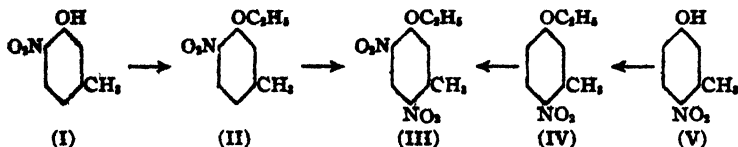
The behavior of our monobromo-6-nitro-*m*-cresol, as has been indicated above, showed that bromine was in position II or IV. If in position 2, the ethyl ether of the monobromodinitro-*m*-cresol described on page 1506 should be identical with the product obtained by bromination of 4,6-dinitro-*m*-cresyl ether, formula (III) above. This ether was prepared and attempts were made to brominate it, but thus far all have failed. If the bromine in our product had been in position IV, then the ether described on page 1503, if it reacts with ammonia when heated in a sealed tube with the latter,[3] should give the nitro bromotoluidin $(NH_2:CH_3:Br:NO_2 = 1:3:4:6)$ described by Nevile and Winther.[4] As will be shown below, the ether in question did not react with ammonia.

The proof that the bromine atom in our product occupies position IV was finally brought in another way. When the compound was chlorinated in the presence of iron as a carrier, one chlorine atom entered and this, as will be shown below, took position II. This monochloromonobromo-6-nitro-*m*-cresol was next reduced to the corresponding amine, and the latter treated with nitrous acid for the purpose of converting it into a diazonium salt which, it was hoped, could be decomposed by cuprous chloride, thus replacing the amino group by chlorine. As will be stated in detail in the experimental part, treatment of the amine with nitrous acid gave a

[1] Duclos, *Ann. Chem. (Liebig)*, 109, 141 (1859).
[2] *Ann. Chem. (Liebig)*, 259, 210 (1890)
[3] Staedel and Orth, *Ann. Chem. (Liebig)*, 259, 210 (1890).
[4] *Ber. d. chem. Ges.*, 13, 972 (1880).

...oxide which was finally made to undergo, but with some difficulty, the Sandmeyer reaction. In this way there was obtained a monobromo-dichloro derivative, the structure of which turned out to be 2,6-dichloro-4-bromo-m-cresol. Oxidation of this product by means of the usual dichromate mixture gave a quinone that contained no bromine and which was found, both by analysis for halogen and by comparison of its melting point[1] with 2,6-dichlorotoluquinone, to be identical with the latter. Taken together these reactions show that in the monobromonitro-m-cresol under investigation the bromine is in position IV, that is, para to hydroxyl. The steps showing the proof of the structure may be briefly summarized as follows:

OH   OH   OH   OH
O₂N⟩   →   O₂N⟩   →   O₂N⟩Cl   →   H₂N⟩Cl   →
   ⟩CH₃   ⟩CH₃   ⟩CH₃   ⟩CH₃
                Br   Br   Br

N—O   O
‖   ‖
N⟩Cl   or   N⟩Cl   →   Cl⟩Cl   →   Cl⟩Cl
  ⟩CH₃   N‖⟩CH₃   OH⟩CH₃   ⟩CH₃
  Br   Br   Br   O
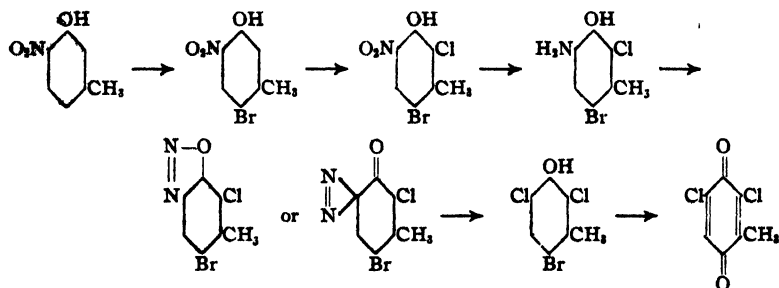
Experimental Part.

The starting point in this work was m-cresol, which was obtained by fractionating a pure commercial product. Fifty grams of the liquid, boiling at 199–200° (uncor.), were nitrated in accordance with the method of Staedel and Orth,[2] and the isomeric nitro compounds that resulted were separated by distillation with steam. The o- compound, 6-nitro-m-cresol, which is volatile under these conditions, was found to melt at 56°, as reported in the literature, and was used without further purification in the experiments described below.

[1] The fact that the product obtained here melted at the same temperature as 2,6-dichlorotoluquinone, and failed to depress the melting point of the latter, was not, alone, accepted as sufficient proof of the identity of the two products. The additional precaution of analyzing the compound in question was taken because we have found that in certain of the toluquinones chlorine may replace bromine without a change of melting point, and that the two products may be melted together without such a depression as would usually be regarded as showing that the products are different. Thus, a mixture of 2,6-dibromotoluquinone (*J. prakt. Chem.*, [2] **39**, 370 (1889); *Am. Chem. J.*, **46**, 430 (1911)), m. p. 117°, and 2-chloro-6-bromo-3-methylquinone (THIS JOURNAL, **36**, 679 (1914)), m. p. 119°, shows no sign of melting below 117°. Likewise, a mixture of p-chlorotoluquinone (*Ber.*, **20**, 2286 (1887)), m. p. 105°, and p-bromotoluquinone (*Ber.*, **27**, 1931 (1894)), m. p. 106°, melts at 103–104°; while a mixture of the corresponding hydroquinones, each of which melts separately at 176°, does not melt below 174°.

[2] *Ann. Chem. (Liebig)*, **217**, 51 (1883).

Action of Bromine on 6-nitro-m-cresol.—A portion of 6-nitro-m-cresol weighing 10.2 g. obtained as specified above, was dissolved in 75 cc. glacial acetic acid, and to this solution there was gradually added from a dropping funnel a solution of 6.7 cc. bromine (enough to convert all nitrocresol into dibromo derivative) in 30 cc. of glacial acetic acid. While the solution was slowly added the flask was frequently shaken. The operation was begun at the room temperature and lasted about one hour, during which time the temperature rose slightly. Crystals began to separate about the time all bromine had been added, and the mixture was allowed to stand for six hours in a cool place in order to secure as large a yield as possible. At the end of this time the crystals were collected on a filter, washed with a small quantity of glacial acetic acid, and dried on a clay plate. Chilling the filtrate increased the yield to 9.5 g., which is about 61% of the possible amount, if all had been converted into the monobromo product. In this condition the compound melted at 123°, and was very nearly pure. It was readily soluble in ether and alcohol, and was best purified by crystallization from the latter liquid, from which it separated in the form of yellow plates that melt at 126°. It may be purified by distillation with steam, though it does not pass over rapidly. It was analyzed for nitrogen by the Dumas combustion method, and for halogen by the Carius method. Both results agree with the formula for a monobromo product.

     0.1803 g. subs. gave 0.1473 g. AgBr; 0 2643 g. subs. gave 14 9 cc N at 749 3 mm. and 24° over 50% KOH solution.

     Calc. for $C_7H_6O_3NBr$: Br = 34.48; N = 6.04, found: 34 76, 6.24.

The filtrate obtained when the monobromo product described above was removed was allowed to stand over night to see if it would deposit more solid. Nothing was deposited. The clear liquid was then poured with stirring into six volumes of ice water, and the precipitate allowed to settle during several hours. The yellow solid, after being collected on a filter and dried on a clay plate, weighed 7.2 g., less than 35% of that required by the theory on the basis of the formation of dibromo compound only. The substance was purified by repeated crystallization from alcohol, and was obtained in the form of yellow needles that melted sharply at 87°. A mixture of this product with 2,4-dibromo-6-nitro-m-cresol, m. p. 87°, obtained by the nitration[1] of 2,4,6-tribromo-m-cresol, melts at the same point as either of them separately, which shows that they are identical. This product, is, also, probably identical with that obtained by Claus and Hirsch[2] by brominating 6-nitro-m-cresol, though they report 93° as the melting point.

Salts of 4-bromo-6-nitro-m-cresol.—The monobromo compound described above reacts readily with bases to form salts. Several of these were stud-

     [1] *Am. Chem. J.*, 46, 427 (1911).
     [2] *Loc. cit.*

ied. The ammonium salt was obtained by allowing the pulverized nitro compound to stand over night with concentrated ammonia water. The solubility of the product in cold water is so slight that the yield of salt obtained by filtering the above mixture was nearly quantitative. The salt was purified by repeated crystallization from dilute ammonia water. It was found, in fact, that the nitro compound could be purified most easily in the form of ammonium salt, which latter could afterward be decomposed by hydrochloric acid. The salt crystallized in the form of orange colored needles.

0.2810 g. subs. gave 0.2138 g. AgBr; 0.2152 g. subs. gave 20.4 cc. N at 731.5 mm. and 21.5° over 50% KOH solution.

Calc. for $C_7H_9O_4N_2Br$. Br = 32.12; N = 11.26; found. 32.37, 10 59.

The potassium salt was prepared by dissolving the nitrocompound in a hot aqueous solution containing slightly more than the theoretical amount of potassium hydroxide, and then allowing the liquid to cool to the room temperature. Five grams of nitro compound gave 4.05 g. of potassium salt which was increased to 5.05 g. by working up the mother liquor. It was purified by two crystallizations from water, and formed deep red needle-shaped crystals.

Analysis for potassium was carried out by igniting the salt with dilute sulfuric acid.

0.2088 g. subs. gave 0.0669 g. K_2SO_4; calc. for $C_7H_5O_3NBrK$: K = 14.44; found: 14.38.

The sodium salt, prepared in the same way as the potassium compound, crystallized from water in red needles.

0.8654 g. subs. gave 0.2446 g. Na_2SO_4. Calc. for $C_7H_5O_3NBrNa$: Na = 9.07; found: 9.13.

The silver salt, which is but sparingly soluble in water, was prepared by adding a slight excess of silver nitrate solution to a solution of the sodium salt that had been purified by several crystallizations, and that was free from any considerable amount of alkali. The dark red precipitate that formed at once was filtered off, washed with water and dried on clay plate. It was used in the preparation of the ethyl ether that is described below.

Ethyl Ether of 4-Bromo-6-nitro-m-cresol.—Five grams of the above de-scribed silver salt were dried and pulverized. This powder was mixed with dry ether and considerably more than the theoretically required amount of ethyl iodide. To hasten and complete the reaction, which appeared to go very slowly at the room temperature, the mixture was heated for five hours under a reflux condenser on the water bath. The mixture was then filtered to remove silver iodide and any unchanged silver salt of the nitro-cresol, and the residue extracted several times with dry ether. The ethereal solution was then shaken with sodium carbonate solution in order to remove any free nitro compound, and after separation from the alkaline

liquid was evaporated to dryness by distilling off the ether. The residue weighed about 2 g. This was purified by crystallization from ligroin, 70–80°, from which it separated in the form of plates having a slight tan color. A second sample was repeatedly crystallized from alcohol, and gave nearly colorless crystals. The m. p. in both cases was 124°, which is very near that of the nitro compound (126°) from which we started. The two products, however, were shown to be different both by melting them together and by analysis. The mixture melted at 97–102°.

0.2472 g. subs. gave 0.1788 g. AgBr. Calc. for $C_9H_{10}O_2NBr$: Br = 30.76; found: 30.78.

The question of the behavior of this ether toward ammonia when the mixture was heated under pressure was next considered. Staedel and Kolb[1] found that the ethyl ether of 6-nitro-*m*-cresol reacted with ammonia under these conditions to replace the ethoxy by the amino group, and that the same reaction took place with the corresponding dinitro and trinitro ethers. Since their mononitro compound corresponded to our product, with the exception that theirs contained no bromine, it was expected that ours would react with ammonia, and, by replacement of the ethoxy group, give a nitrobromotoluidin ($NH_2:CH_3:Br:NO_2 = 1:3:4:6$) of known structure.[2] A portion of our product was mixed with concentrated aqueous ammonia, and heated in a sealed tube for eight hours at 150°. Nothing but the unchanged ether was recovered from the reaction mixture.

Hydrochloride of 4-Bromo-6-amino-m-cresol.—This compound was obtained by dissolving 5 g. of the corresponding nitro compound in boiling alcohol, and adding to the boiling liquid a solution of stannous chloride in concentrated hydrochloric acid. When reduction was complete, one volume of concentrated acid was added and the mixture allowed to come to the room temperature. The amino hydrochloride that separated was removed by filtration and purified as follows: The solid was dissolved in a small quantity of hot water, the solution filtered through paper, and the filtrate mixed with an equal volume of concentrated hydrochloric acid. Nearly colorlesss needle-shaped crystals, that were free from tin compounds were obtained.

0.2496 g. subs. gave 0.3476 g AgHal; calc for $C_7H_9ONClBr$: halogen = 48.41; found: 48.51.

4-Bromo-6-amino-m-cresol.—This free base was easily prepared by mixing with a faintly acid (hydrochloric) solution of the aminohydrochloride, described above, a slight excess of ammonium carbonate solution. The amine was promptly precipitated, and after a few minutes it was collected on a filter, washed several times with cold water, and dried on clay plate. It was found to be soluble in alcohol, benzene, and less so in ligroin. It

[1] *Ann. Chem. (Liebig),* 259, 224 (1890).
[2] *Ber.,* 13, 972 (1880).

was best purified by crystallization from benzene, from which it was obtained in nearly colorless crystals that melted sharply at 145°.

0.1532 g. subs. gave 0.0808 g. Ag (electrolyt. dep.); calc. for C_7H_8ONBr: Br = 39.55; found: 39.04.

Nitration of 4-bromo-6-nitro-m-cresol.—A portion of the monobromo product weighing 5 g. was finely powdered and then added to a mixture of 54 cc. nitric acid (sp. gr. 1.42) and 21 cc. sulfuric acid (sp. gr. 1.84), that had been cooled to the room temperature. After being shaken for about 15 min. the reaction mixture was filtered through glass wool to remove unchanged material, and the clear filtrate was poured into ten volumes of cold water. A light yellow precipitate was formed. The liquid was allowed to stand for half an hour, after which the solid was removed by filtration, washed with a little cold water, and dried on clay plate. In this condition the product melted at 72°–75°, due to the presence of trinitro-m-cresol, probably. To show that the latter had been formed during the nitration, some of the filtrate obtained as above was extracted with ether, the ether removed by evaporation, and the residue dissolved in water and converted into potassium salt. The latter was twice crystallized from water and then decomposed by hydrochloric acid. The free nitro compound was removed and crystallized from alcohol. It was melted with a sample of trinitro-m-cresol prepared in accordance with the method of Duclos,[1] without showing any depression of melting point. To show that the monobromomononitro compound could be easily and completely converted into trinitro-m-cresol in a single operation, a portion was nitrated by varying the above method slightly. In this case the reaction mixture was warmed sufficiently to bring all solid into solution, and when the latter was poured into water nothing was precipitated. Extraction with ether and purification as described for the filtrate above gave a compound that melted sharply at 106°, and that did not depress the melting point of a sample known to be trinitro-m-cresol.

In order to secure the dinitro compound in a pure form, the crude product melting at 72°–75° was converted into ammonium salt, and this was repeatedly crystallized from ammonium hydroxide solution. Orange colored crystals were obtained.

0.2798 g. subs. gave 0.1802 g. AgBr; calc. for $C_7H_8O_5N_2Br$: Br = 27.22; found: 27.40.

A portion of the pure ammonium salt was dissolved in water and then a slight excess of hydrochloric acid added. The free nitro compound that separated was collected on a filter, dried in the air, and crystallized twice from ligroin, 70°–80°. It gave fine yellow needles that melted sharply at 77°.

0.1287 g. subs. gave 0.0868 g. AgBr; calc. for $C_7H_6O_5N_2Br$: Br = 28.88; found: 28.70.

[1] *Ann. Chem. (Liebig)*, 109, 141 (1859).

Potassium Salt of 4-Bromo-2,6-dinitro-m-cresol.—The dinitro compound that has been described was further identified by the preparation of its potassium salt. The other reason for preparing this salt was to secure material for the preparation of the ether mentioned below. The salt was easily obtained by dissolving the nitro compound in a slight excess of hot potassium hydroxide solution, from which the product separated in scarlet plates which were further purified by a second crystallization from water.

^{1} 0.2849 g. sub. gave 0.1711 g. AgBr; calc. for $C_7H_4O_5N_2BrK$: Br = 25.59; found: 25.55.

Silver Salt of 4-Bromo-2,6-dinitro-m-cresol.—The silver salt was prepared by mixing slightly more than the calculated amount of silver nitrate solution with a warm dilute solution of the potassium salt described above. Scarlet crystals of the silver salt formed rapidly. These were removed by filtration, washed with a small quantity of cold water, and then dried. It may be noted that this salt is much more soluble in water than the silver salt of the mononitro compound, mentioned on a previous page. It was used in the preparation of the ethyl ether.

Ethyl Ether of 4-Bromo-2,6-dinitro-m-cresol.—This ether was prepared for the purpose of securing a substance having the same composition and containing the same groups as the expected bromine derivative of the 4, 6-dinitro-*m*-cresyl ether (p. 1500), which we were trying to obtain at that time, with the hope that a comparison of the properties of the two products would enable us to decide the position of the bromine atom. Though the failure of bromine to react with the dinitro ether prevented the comparison, it seemed worth while to report the preparation of the ether here described in order to call attention to the marked difference in the rates of reaction when the silver salts of 4-bromo-6-nitro-*m*-cresol, and 4-bromo-2,6-dinitro-*m*-cresol, respectively, were brought in contact with ethyl iodide. The first named, as has been pointed out above, reacted very slowly; the second, as indicated below, reacted rapidly. Three grams of the silver salt of monobromodinitro-*m*-cresol were mixed with 20 cc. of dry ether, and then slightly more than the calculated amount of ethyl iodide was added. Vigorous action began at once, with considerable rise of temperature, and the reaction was apparently complete in a short period (few minutes). Heating the mixture under a reflux condenser over a water bath caused no further change. The cooled mixture was filtered, the residue washed several times with small portions of dry ether, and the collected filtrate and washings shaken with a solution of sodium carbonate for the purpose of removing any free nitro compound. When the ethereal solution was placed in a distilling flask and the ether evaporated off, a brown, syrupy liquid was left. This was cooled with ice, but it failed to give any solid until allowed to stand for several hours in a vacuum desiccator. The brown solid finally obtained was crystallized from methyl alcohol, and gave

nearly colorless crystals that melted at 64°–65°. The substance becomes yellow colored when kept. It was easily soluble in other organic solvents, but did not crystallize well from any but alcohol.

0.2223 g. subs. gave 0.0785 g. Ag (electrolyt dep); calc for $C_9H_7O_4N_2Br$: Br = 26.25; found: 26.16.

The Action of Bromine on the Monobromo-6-nitro-m-cresol.—A portion of the monobromonitrocresol weighing 2 g. was dissolved in 15 cc. glacial acetic acid, and the solution warmed slightly. To this, a solution of bromine in acetic acid was added, and after being shaken for a few minutes, was cooled. No crystals of monobromo compound separated out. The liquid was poured, with stirring into six volumes of cold water, and gave a yellow precipitate. This was removed by filtration, dried, and, crystallized from alcohol. Long yellow needles that melted at 87° were obtained. When a mixture of this product and the 2,4-dibromo-6-nitro-*m*-cresol obtained by the nitration of 2,4,6-tribromo-*m*-cresol was melted, the melting point was the same as that of either product separately, which indicates that they are identical. In the monobromo compound under investigation, then, bromine occupied position II or IV.

Chlorination of the Monobromo-6-nitro-m-cresol.—The first attempts to chlorinate this compound were made by passing chlorine into a glacial acetic acid solution of the substance. The yield was poor and the product was difficult to purify. A much better result was obtained by using carbon tetrachloride as a solvent and dry pulverized iron as a "chlorine carrier." Ten grams of the compound were dissolved in 290 cc. carbon tetrachloride, and about 2 g. of iron added. One molecule of chlorine, generated by dropping hydrochloric acid on potassium permanganate, was led into this liquid, while the flask was continually shaken. The temperature did not rise much above that of the room. At the end of the reaction the mixture was filtered through paper, and the clear filtrate reduced to a small volume by distilling off the carbon tetrachloride on the water bath. The dark colored residue was poured into a beaker and allowed to crystallize while the remainder of the solvent slowly evaporated. The solid weighed 11.2 g. and had a m. p. of 72°–75°. The compound dissolves readily in alcohol, and after four crystallizations from that solvent it had a constant m. p. of 80°. It can be purified quite easily in the form of its potassium salt, which separates from water in the form of crimson rhombic crystals. A second crystallization in this way gave a product that was shown by analysis to be pure.

0.3395 g subs. gave 0.3691 g. AgHal; calc for $C_7H_4O_3NClBrK$: Hal = 37.92; found: 37.87.

The free nitro compound, which turned out to be 2-chloro-4-bromo-6-nitro-*m*-cresol, was obtained from the potassium salt described above by treatment of an aqueous solution of the latter with hydrochloric acid.

The yellow precipitate was collected on a filter, washed with water, and at once crystallized from alcohol. It gave yellow needles that melted at 80°. It should be noted that a mixture of this compound and dichloro-6-nitro-*m*-cresol, m. p. 88°,[1] in which the halogen atoms are probably in positions II and VI, does not melt below 80°.

0.2089 g. subs gave 0.2584 g. AgHal; calc for $C_7H_6O_3NClBr$: Hal = 43.31; found: 43.11.

Hydrochloride of 2-Chloro-4-bromo-6-amino-m-cresol.—The nitro compound under consideration was further identified by the preparation of the corresponding aminohydrochloride. This was done in the manner already described, though it was found necessary to use much more alcohol than has been required in the cases of other nitro compounds.[2] This was due to the fact that both the nitro compound and the hydrochloride are almost insoluble in the hydrochloric acid used to dissolve the stannous chloride employed in the reduction. Consequently, unless enough alcohol is used to hold all nitro compound in solution, at the boiling point, even when it is diluted with an equal volume of an aqueous liquid, reduction will not be complete, and the solid that separates when the mixture cools will contain both nitro compound and aminohydrochloride. The very slight solubility of the hydrochloride in water made it necessary to modify the method described above for purifying these compounds. This one was best freed from tin salt by treatment of its solution in dilute alcohol with concentrated hydrochloric acid. The nearly colorless crystals that resulted were collected on a filter, pressed out on a porous plate and dried in air 24 hours, and then *in vacuo*, over potassium hydroxide, for 72 hrs. before analysis.

0.2561 g. subs. gave 0.4413 g. AgHal; calc. for $C_7H_8ONCl_2Br$: Hal = 55.28; found: 54.80.[3]

2-Chloro-4-bromo-6-amino-m-cresol.—The free base was obtained by decomposing the hydrochloride with ammonium carbonate. After washing with water and drying over night the base was crystallized from benzene. It gave nearly colorless scales that melted at 145°–146°. With acetic anhydride it reacts very vigorously to give a derivative that crystallized from alcohol in the form of long, colorless, silky needles that melted at 199°. This substance did not dissolve in solution of sodium hydroxide except on standing for several hours, and was regarded as a diacetyl com-

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[1] Raiford and Baird, unpublished work.

[2] *Am. Chem. J.*, **46**, 419 (1911).

[3] The low percentage of halogen was not regarded as indicating an impure substance, because in a closely related case (THIS JOURNAL, **36**, 678 (1914)) the same facts were noted, while in that case, as in this, the free base (see below) obtained from the hydrochloride was found by analysis to be pure. The explanation of the low percentage of halogen in both hydrochlorides is the probable loss of hydrogen chloride by dissociation during the drying.

pound. A portion of the free base was dried *in vacuo* for 24 hrs., and analyzed.

0.2648 g. subs. gave 0 3722 g. AgHal, calc for $C_7H_7ONClBr$ Hal = 48 82; found · 48.98.

Reaction of 2-Chloro-4-bromo-6-amino-m-cresol with Nitrous Acid.—In order to secure further proof of the position of the bromine atom in the compound under consideration, it was proposed to replace the amino group by chlorine, by means of the Sandmeyer reaction, and then try to oxidize the resulting cresol to the corresponding quinone. In such a case the halogen para to hydroxyl would be lost, and identification of the quinone would show whether chlorine or bromine occupied the *p*- position in the original substance. The preliminary attempts to diazotize the amine did not give satisfactory results. In the first place, the aminohydrochloride with which we started is nearly insoluble in water, and particularly so in the presence of the relatively large amount of hydrochloric acid necessary for the Sandmeyer reaction. Attempts to secure a paste by grinding the solid with water and acid did not give a homogeneous mixture. It was therefore found impossible to bring the sodium nitrite solution in contact with this material, and secure a uniform reaction, by agitating the containing flask in the usual way. This difficulty was further emphasized by the fact that the product of the reaction (which was not a diazonium salt) was quite as insoluble in water as the compound with which we started. To overcome these unfavorable conditions, in a measure, the mixture of aminohydrochloride, water and hydrochloric acid, after being rubbed into as smooth a paste as possible, was placed in a glass stoppered bottle; and after each addition of the sodium nitrite solution the bottle was removed from the cooling bath and shaken vigorously for several minutes. When, after such a mixing of the material, a test showed the presence of free nitrous acid, a portion of the brown solid was removed by filtration, washed with water and dried. It decomposed suddenly when heated above 155°. After two crystallizations from alcohol it was obtained in the form of brown needles that behaved as stated above. These properties indicated a diazo-oxide, and an analysis for halogen supported this view.

0.1995 g. subs. gave 0.2673 g. AgHal; calc. for $C_7H_4ON_2ClBr$: Hal = 46.65; found: 46.70.

Behavior of the Diazo-oxide toward Cuprous Chloride Solution.—Portions of the mixture containing the diazo-oxide were transferred in the usual way to the amount of cuprous chloride solution commonly employed in the Sandmeyer reaction. The yield was poor, and the product was a mixture that we did not succeed in separating. Only when 2.5 to 3.0 times the usual quantity of cuprous chloride solution was used, and when, after each addition of liquid containing the diazo-oxide, the mixture, contained

in a stoppered bottle, was vigorously shaken for several minutes, was a satisfactory yield of fairly pure product obtained. Without these precautions the diazo-oxide tends to float on the surface of the liquid and escape action with the cuprous chloride. After mixing, the liquid was allowed to stand for half an hour, with frequent shaking, and was then distilled with steam. An oil that solidified partly in the condenser passed over. Cooling the receiving flask caused the entire product to solidify in the form of crystals that were slightly brownish in color. These were collected by filtration, and dried. The yield was about 65% and the substance melted at 63–64°. It was further purified by crystallization from ligroin (70°–80°), from which it separated in pale, fawn colored needles that melted at 65°. It is but sparingly soluble in water, and the solution develops no color when mixed with ferric chloride.[1] It is readily soluble in solution of sodium hydroxide, and from this it is completely precipitated by carbon dioxide. It cannot be distilled at atmospheric pressure without decomposition. Analysis for halogen showed that it is a monobromodichlorocresol.

0.2141 g. subs. gave 0.3986 g. AgHal; calc. for $C_7H_5OCl_2Br$: Hal = 58.90, found 59.17.

Oxidation of 2,6-Dichloro-4-bromo-m-cresol.—One gram of the cresol was dissolved in 30 cc. glacial acetic acid, and the solution cooled as far as possible (to about 10°) without causing solid to separate. To this liquid there was gradually added, with shaking, a cold solution of sodium dichromate and sulfuric acid, and the mixture allowed to stand for half an hour. An equal volume of cold water was next added and the whole left for an hour. The quinone that subsided was removed by filtration, washed well with cold water, and dried. A yield of about 65% was obtained. In this condition the product melted at about 90°. After crystallization from ligroin (70–80°) it melted at 102°, and a mixture of it and 2,6-dichlorotoluquinone, obtained by oxidizing 2,4,6-trichloro-m-cresol in the manner described above, showed no depression. A small quantity of the substance was mixed with water and reduced by sulfur dioxide to the corresponding hydroquinone. This melted at 171°, and did not depress the melting point of 2,6-dichlorotoluquinone.[2] These facts, however, were not sufficient to establish, beyond question, the identity of the two products; for it has been found, as stated on a previous page, that in this group, at least, chlorine and bromine may replace each other without causing a change of melting point, and that the respective products may be melted together without appreciable depression. Our product, therefore, was analyzed.

0.1575 g. subs. gave 0.2378 g. AgCl; calc. for $C_7H_4O_2Cl_2$: Cl = 37.14; found: 37.33.

[1] See *Am. Chem. J.*, 46, 424 (1911).

[2] *Ber.*, 19, 931 (1886).

,   Summary.   ,

1. When 6-nitro-*m*-cresol is brominated in acetic acid solution, a mixture of 4-bromo-6-nitro-*m*-cresol and 2,4-dibromo-6-nitro-*m*-cresol is formed. The difference in solubility of these two products in acetic acid permits of almost complete separation by filtration of the reaction mixture. 4-Bromo-6-nitro-*m*-cresol, which had not previously been described, has been studied and its structure established.

2. The ortho positions of the hydroxyl and nitro groups in the mononitrodibromo-*m*-cresol (m. p. 87°) obtained by nitration of 2,4,6-tribromo-*m*-cresol[1] have been confirmed.

3. When 4-bromo-6-nitro-*m*-cresol is chlorinated in the presence of iron, chlorine enters position II, that is, between methyl and hydroxyl.

4. Treatment of 2-chloro-4-bromo-6-amino-*m*-cresol with nitrous acid gives a diazo-oxide that will react with cuprous chloride to give a trihalogenated cresol.

CHICAGO, ILL.

THE ACTION OF CHLORAL, CHLORAL HYDRATE AND BROMAL ON CERTAIN ORGANIC COMPOUNDS IN THE PRESENCE OF ALUMINIUM CHLORIDE.

BY G. B. FRANKFORTER AND W. KRITCHEVSKY.

Part 1.

The following pages are devoted to a new phase of the Friedel-Crafts reaction. This unique historical reaction[2] represents one of a series of chemical changes commonly classed under catalysis. Catalysis may be best defined as a chemical change, either analytic or synthetic, brought about by the influence of a substance but without that substance entering permanently into the reaction; or, as stated by Ostwald, an increase in the reaction velocity beyond the normal by some substance which does not enter the reaction.

As is well known, many of the true organic condensation processes are brought about by one of two common reactions, namely, the Friedel-Crafts and the Baeyer reaction, the one acknowledged as purely catalytic, eliminating hydrochloric acid—the other, perhaps dehydrolytic, eliminating water. It will be shown in this paper that although these two reactions have been regarded as separate and distinct in their behavior ever since they were discovered by the men whose names they bear, they do, in many cases, act alike; for aluminium chloride not only plays the part of a catalyst in breaking off hydrochloric acid, but it also acts as a substitute for sulfuric acid, removing water from the reacting components.

[1] *J. prakt. Chem.*, [2] **61**, 561 (1900); *Am. Chem. J.*, **46**, 426 (1911).

[2] *Compt. rend.*, **84**, 1392 (1877); *Ann. chim. phys.*, [6] 449 (1884).

It may be of some historic interest to note that Playfair was doubtless the first to show the catalytic properties of aluminium. He found that if a piece of calico dyed in indigo be dipped in nitric acid, no change takes place; but if the nitric acid contains a mere trace of an aluminium salt, the blue color is immediately destroyed.

It was found by Friedel and Crafts that, when small quantities of anhydrous aluminium chloride were added to amyl chloride, a vigorous reaction took place, liberating hydrochloric acid, at the same time forming hydrocarbons which did not absorb bromine. The reaction seemed deep seated, but one of the compounds formed was a hydrocarbon of the general formula, C_nH_{2n+2}, thus indicating that a different hydrocarbon of the same group had been formed. Finally, when the above reaction was made to take place in the presence of a hydrocarbon, a compound consisting of the hydrocarbon and the amyl radical was formed. By substituting other halides, as methyl or ethyl chlorides, homologous compounds were formed. No definite explanation was at first given. The reaction was so unusual that the discoverers seem to have been content to accept the reaction as fact and wait for more data before attempting an explanation.

In addition to the work of the authors themselves, Gustavson[1] did much toward an explanation of the reaction. He showed that organic aluminium compounds of unstable nature are formed and that these compounds readily break down, liberating the condensed hydrocarbon with the reformation of aluminium chloride.

Since Friedel and Crafts' first experiments with aluminium chloride, chemists have used it in many different ways for bringing about different chemical changes. Thus, Scholl and Seer[2] showed that anhydrous aluminium chloride in many cases actually breaks off hydrogen instead of hydrochloric acid, as may be shown by the following equation:

$$C_5H_{12} + Al_2Cl_6 = C_5H_{10} + H_2 + Al_2Cl_6$$

They did not attempt to explain this reaction, but, from organic aluminium compounds which we have had in hand, it seems quite probable that the first substance formed is an aluminium compound as indicated by the following equation:

$$C_5H_{12} + Al_2Cl_6 = C_5H_{11}Al_2Cl_5 + HCl$$

Then the hydrogen ion of the acid breaks the aluminium alkyl down, liberating the hydrogen and reforming aluminium chloride according to the following equation:

$$C_5H_{11}Al_2Cl_5 + HCl = C_5H_{10} + Al_2Cl_6 + H_2$$

[1] *Bull. soc. chim.*, **42**, 325 (1884); *Ber.*, **13**, 157 (1880).
[2] *Monatsh.*, **33**, 1 (1912).

Page[1] has recently shown that anhydrous aluminium chloride possesses the power of transporting chlorine to organic compounds. In a very few cases, we have suspected it of having similar properties, although the evidence at hand is not entirely conclusive.

Another reaction which is more or less closely related to those described below, is the synthesis of anthraquinone from phthalic anhydride and benzene, by means of aluminium chloride and sulfuric acid. At first glance the chloride might be regarded as a dehydrating agent. A careful examination will show, however, that the reaction brought about by aluminium chloride is not condensation at all but an addition reaction, dehydration being brought about by means of concentrated sulfuric acid, as may be shown by the following equation:

$$C_6H_4{<}^{CO}_{CO}{>}O + C_6H_6 + Al_2Cl_6 = C_6H_4{<}^{CO}_{COOH}C_6H_5 + Al_2Cl_6$$
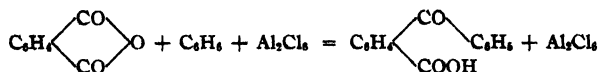
The final reaction in which a molecule of water was removed was brought about by means of sulfuric acid:

$$C_6H_4{<}^{CO}_{COOH}C_6H_5 + H_2SO_4 = C_6H_4{<}^{CO}_{CO}{>}C_6H_4 + H_2O + H_2SO_4$$
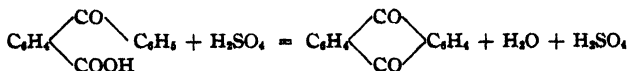
Experimental Part.

The first experiments in which it was observed that aluminium chloride had dehydrating properties were made by one of us and Poppe[2] with pinene, chloral and aluminium chloride. These substances, when brought together at the ordinary room temperature undergo an extremely complex reaction, forming, as one of the condensation reactions, substances which do not contain oxygen. It was naturally inferred that in this part of the reaction, pinene and chloral must have combined through the elimination of water. Just how the reaction takes place has not yet been determined with absolute certainty. The natural inference is, however, that aluminium chloride in some part of the reaction plays the part of a dehydrating reagent. Following out the assumption that water is eliminated from pinene and chloral by aluminium chloride, the various groups of organic compounds were substituted for pinene. In each case theory became fact, for in each case the chloride acted as a plain dehydrating reagent.

Our first experiments with anisol and phenetol, chloral and aluminium chloride showed, as was suspected in our work on the terpenes, that the latter acts exactly like concentrated sulfuric acid in removing a molecule of water and forming a trihalogen condensation product. Some of this

[1] Ann., 225, 196 (1884).

[2] Contribution to Our Knowledge of the Terpenes; Frankforter and Poppe. Read before International Congress of Applied Chemistry, New York, 1912.

series of compounds had been previously prepared by the Baeyer or sulfuric acid reaction. None, however, had been prepared by means of aluminium chloride. In fact, a number of these ether derivatives were prepared for the first time by the aluminium chloride method and reported by us at the Eighth International Congress of Applied Chemistry at New York, 1912.

Experimental work soon showed that this peculiar action of aluminium, chloride is by no means confined to the phenol ethers. On the contrary it appeared to be almost as universal in its application as a dehydrating reagent as sulfuric acid. We have used it in preparing condensation products of the aliphatic, the benzene, the naphthalene and the anthracene series, not only with chloral but also with chloral hydrate and bromal.

General Method of Preparation.—In the preparation of the compounds which appear in this paper, the reactions were practically all brought about in the same manner. The two reacting components were first mixed and after cooling to zero or below, aluminium chloride was added in small portions and the whole allowed to stand for 24 to 72 hrs. in a freezing mixture. In each case the reaction seemed to have been completed within the above mentioned time limits. After the reaction had been completed, the whole mass was washed with water and distilled with steam in order to remove the unchanged reacting components. The condensation product was, in most cases, removed by extracting with ether from which it usually crystallized. Those substances which refused to crystallize from ether were invariably found to crystallize from chloroform or alcohol. In a very few cases the substance could only be obtained in a semi-crystalline form, in which case the constant melting point was regarded as sufficient evidence that the substance was pure enough for analysis. In a few cases the substance had to be distilled *in vacuo* before it would crystallize from ether, alcohol or any other organic solvents.

Condensation of the Aliphatic Hydrocarbons, Chloral and Aluminium Chloride.—Pentane and chloral react vigorously when brought together in the presence of aluminium chloride. So extremely violent is the reaction that, even at a freezing temperature it is complex, giving as a result several substances, none of which has been obtained quite pure enough for analysis. It is evident, however, that the condensation reaction takes place eliminating a molecule of water. This and other experiments with the aliphatic compounds are under investigation.

Condensation of the Aromatic Hydrocarbons, Chloral and Aluminium Chloride.—It was found that the aromatic hydrocarbons, when treated with chloral in the presence of aluminium chloride, formed the same condensation products obtained by other condensation reagents. Thus, benzene, toluene and xylene gave their own characteristic condensation compounds according to the common equation:

$$2RH + OCH-CCl_3 + Al_2Cl_6 = R_2CH-CCl_3 + H_2O + Al_2Cl_6,$$

when R represents the phenyl, toluyl and the xylyl groups.

It should be stated here that benzene, chloral and aluminium chloride have recently been studied, but different investigators have obtained entirely different results. Thus, Combes,[1] by treating 1000 g. of benzene with 200 g. of chloral and 40 g. of aluminium chloride, obtained an extremely complex reaction. No less than four different substances were isolated:

1. Diphenylchloral hydrochloride, $(C_6H_5)_2CH-CCl_3HCl$ (liquid with an aromatic odor).
2. Diphenyldichloroethane, $(C_6H_5)_2CHCHCl_2$, solid, m. p. 74°.
3. Compound of unknown composition, $C_{22}H_{17}Cl$, solid, m. p. 83°.
4. Tetraphenylethane, $(C_6H_5)_2CH-CH(C_6H_5)_2$.

Biltz[2] obtained the following results by treating benzene and chloral with aluminium chloride:

1. Tetraphenylethane, $(C_6H_5)_2CH-CH(C_6H_5)_2$, solid, m. p. 207°.
2. Diphenyldichloroethylene, $(C_6H_5)_2C=CCl_2$, solid, m. p. 80°.
3. Triphenylvinyl alcohol, $(C_6H_5)_2C=C(OH)C_6H_5$, solid, m. p. 136°, and a substance of unknown composition with a melting point of 233°.

Böeseken[3] very recently (since an abstract of this paper was read at the 8th International Congress) repeated the work of Combes and Biltz. He explained the reaction by assuming that diphenylmethane and chloroform are formed. This work was not absolutely proven, as he himself states.

Of equal interest, along this line, is the work of Dienesmann,[4] who, upon treating 1000 g. of benzene with 200 g. of chloral and 40 g. of aluminium chloride in the cold, obtained a reaction which he expressed as follows:

$$C_6H_6 + OCH-CCl_3 = C_6H_5(OH)CH-CCl_3$$
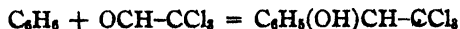
In other words, Dienesmann obtained the aldol reaction in which a secondary alcohol is formed. It is interesting to note that this compound is doubtless the same which Jotsitch[5] obtained by means of the Grignard reaction.

Dienesmann's reaction is of special interest because he worked under conditions somewhat similar to those under which we have worked. The results obtained, however, were entirely different. This is rather strange, because the only difference in the experimental work seems to be the fact that he took a large excess of benzene while we took exactly two

[1] *Bull.*, **45**, 226 (1886).
[2] *Ber.*, **26**, 1952 (1893).
[3] *Chem. Zentr.*, **1912**, I, 897.
[4] *Compt. rend.*, **141**, 201 (1905).
[5] *J. Russ. Phys. Chem. Soc.*, **34**, 96 (1902).

molecules. He kept the reacting substances cool (he does not state how cool) while we kept the temperature down to zero or below. In our experiments the aldol reaction did not take place and the secondary alcohol was therefore not formed. On the contrary, we obtained a simple condensation reaction.

A glance at the Dienesmann reaction will show that it represents what one would expect from either the Friedel-Crafts or of the Grignard reaction. It is at least interesting to note that we have obtained quite different results from those obtained by Dienesmann by simply changing the conditions under which the reaction takes place, namely, changing the proportions of the reacting components and the temperature. From the important work of Dienesmann and from the experiments which follow, it is evident that aluminium chloride, under one set of conditions, acts as a simple catalyst, while under different conditions it plays the part of a dehydrating reagent.

The following table will show the relationship between the Grignard, the Friedel-Crafts and the Baeyer reactions as compared with the one given in this paper.

<div align="center">Grignard</div>

$$C_6H_6 + Mg + I_2 + OCH-CCl_3 = C_6H_5CH(OH)CCl_3 + MgI_2$$

<div align="center">Friedel-Crafts</div>

$$C_6H_6 + OCH-CCl_3 + Al_2Cl_6 = C_6H_5-CH(OH)CCl_3 + Al_2Cl_6$$

<div align="center">Baeyer.</div>

$$2C_6H_6 + OCH-CCl_3 + H_2SO_4 = (C_6H_5)_2CH-CCl_3 + H_2O + H_2SO_4$$

<div align="center">Frankforter-Kritchevsky.</div>

$$2C_6H_6 + OCH-CCl_3 + Al_2Cl_6 = (C_6H_5)CH-CCl_3 + H_2O + Al_2Cl_6$$
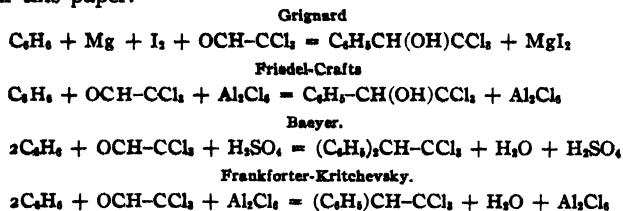
Benzene, Chloralhydrate and Aluminium Chloride.—Benzene reacts with chloralhydrate in the presence of aluminium chloride almost as vigorously as does pentane, so that it was also necessary to bring the reaction about at a low temperature. The first experiment was carried out as follows: 50 g. of pure benzene (2 mol), 57 g. of chloralhydrate ($1^1/_4$ mol) were cooled down to zero, and with constant shaking 10 g. of aluminium chloride added piecemeal. As in the case of pentane, hydrochloric acid was liberated and the whole changed to a light blue color. After allowing it to stand for 48 hrs. the whole mass was poured into water and distilled with steam. The unchanged benzene passed over with the steam. It was found that only a comparatively small quantity of benzene had been acted upon by the chloralhydrate as most of the benzene was recovered and the residue appeared to be unchanged chloralhydrate and aluminium chloride. The experiment was repeated, using the same amounts of benzene and chloralhydrate but increasing the aluminium chloride to one-half molecule. Again a considerable quantity of the benzene remained unchanged. There was left in the flask, however, in addition to the chloralhydrate and

aluminium chloride a thick black oil which did not appear in the first experiment, but the amount was too small for further investigation.

The above experiments were again repeated, using a large amount of aluminium chloride in order to show whether or not the quantity of chloride in any way changed the reaction. The same amounts of benzene and chloralhydrate were taken but the aluminium chloride was increased to 175 g., and added piecemeal as before, to the cooled benzene. During the adding of the chloride, which extended over four hours, the temperature was not allowed to rise above zero. Again, a large amount of hydrochloric acid passed off and the whole mass changed, taking on a deep blue color. After all the chloride had been added the whole mass was allowed to stand 48 hrs. in a refrigerator. During this time more hydrochloric acid was liberated. Ice-water was then added and the mixture allowed to stand for some time. The whole was finally distilled with steam. The steam distillate contained only a small amount of benzene and a small quantity of an oil which had a higher boiling point than benzene, thus indicating that the increase of aluminium chloride had increased the reaction. The residue in the flask, consisting of a thick, dark oil, was washed with water and extracted with ether. The ether solution had a deep greenish fluorescence. The mixture, containing both the ether and aqueous solutions, was washed with sodium hydroxide and finally with dilute hydrochloric acid. The ether solution was then separated from the aqueous part, dried over calcium chloride and the ether allowed to evaporate. The residue left, after evaporating off the ether, was a black, oily liquid. An examination indicated that it was a mixture of several substances. In order to separate them the oil was subjected to fractional distillation *in vacuo*. The first part of the distillate passed over almost colorless at 180° and 55 mm. pressure. It had a distinctly aromatic odor. It was soluble in all the common organic solvents, but refused to crystallize from any of them. It was carefully studied and analyzed. Both physical properties and analysis correspond exactly with the compound, $C_6H_5CCl_2-CHO.HCl$, which Combes[1] prepared. In this part of the reaction, therefore, aluminium chloride apparently played the part of a catalyst as indicated by the following equation:

$$C_6H_6 + CCl_3CHO + Al_2Cl_6 = C_6H_5-CCl_2CHO.HCl + Al_2Cl_6.$$
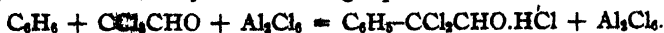
Fractional distillation was continued when the second part distilled over between 220° and 245°. Most of it solidified in the condenser in the form of fine crystals. It was removed and recrystallized from alcohol and ether. After crystallization, it appeared as well-formed, transparent crystals with a melting point of 63–64°. It corresponds exactly with diphenyltrichlorethane, $(C_6H_5)_2CH-CCl_3$, which Baeyer[2] obtained by the

[1] *Bull.*, **45**, 226 (1886).
[2] *Ber*, **5**, 1098 (1873).

condensation of benzene with chloral by means of concentrated sulfuric acid. Analysis also confirmed the reaction.

It is evident from the results obtained that aluminium chloride played a double role. In the formation of the above-mentioned hydrochloride, its action is not unlike the Friedel-Crafts catalysis. In the formation of the diphenyl compound, however, it acts exactly like concentrated sulfuric acid.

Toluene, Chloral and Aluminium Chloride.—It was found that chloral reacted with toluene in the presence of aluminium chloride, forming a condensation product similar to its reaction given above with benzene. 300 g. of toluene were treated with 300 g. of chloral and 175 g. of aluminium chloride under the same conditions mentioned under benzene, and finally distilled *in vacuo*. An oil passed over at 170–180° under 30 mm. pressure with some hydrochloric acid. The oil was dissolved in a mixture of alcohol and ether and allowed to stand, when well-formed, transparent crystals separated out. Recrystallized, it had a m. p. of 88°.

Analysis gave the following   C, 61 20, H, 4.82, and Cl. 33.5.

These analyses, with the physical properties of the substance, leave no doubt that it is *p*-ditoluyltrichloroethane, $(CH_3-C_6H_4)_2CHCCl_3$, prepared by Fischer from toluene, chloral and concentrated sulfuric acid.

p-Toluyldichloroacetaldehydehydrochloride.—During the process of distillation in preparing the ditoluene compound, an oil passed over in addition to the crystals already described. It was carefully studied and found to be a homolog of the Combes benzene derivative. It therefore has the following formula:

$$CH_3.C_6H_4-CCl_2CHO.HCl.$$

We are unable to satisfactorily explain the structural formula of this peculiar compound, the benzene derivative of which was prepared by Combes,[1] who represents the one which he isolated by the above general formula. We hope in the near future to carefully study the structure of these peculiar compounds.

Xylene, Chloral and Aluminium Chloride.—Following the same process used in the preparation of the benzene and toluene condensation products, xylene was treated with chloral in the presence of aluminium chloride. One hundred grams of xylene, 98 g. chloral and 80 g. of aluminium chloride were brought together as in previous experiments, and finally distilled *in vacuo*. A perfectly clear oil with an aromatic odor distilled over between 190 and 220°, at 25 mm. pressure. It readily changed over to crystals, which, after recrystallization from alcohol, had a melting point of 106°. A careful examination, including analyses, showed that the substance was identical with *m*-dixylyltrichloroethane prepared by Elbs from xylene, chloral and sulfuric acid. In this case, however, only one substance, the

[1] *Loc. cit.*

one mentioned above, was formed. Hence, aluminium chloride did not play the role of the Friedel-Crafts catalytic agent.

Cymene, Chloral and Aluminium Chloride.—Cymene was also treated in the usual way with chloral and aluminium chloride, but was found to react quite differently from any of the other hydrocarbons, doubtless owing to its peculiar relationship to the terpenes.   50 g. of cymene (2 mol), 30 8 g. of chloral and 25 g. of aluminium chloride were brought together under exactly the same conditions as in the other hydrocarbons, and finally subjected to fractional distillation under diminished pressure.

The first distillate which passed over was a thick liquid at 220° and at 33 mm. pressure.   The product, before subjecting to distillation, was doubtless an organic aluminium compound, which was found to be soluble in both alcohol and ether but which refused to crystallize from either. The distillate contained no aluminium and only a trace of chloral.   It proved to be an unsaturated compound absorbing bromine with great avidity.   None of the derivatives formed, however, could be obtained in pure enough form for analysis.

Condensation of Alcohols, Phenols and Phenol Ethers with Chloral, Chloral Hydrate and Bromal by means of Aluminium Chloride.

Alcohol, Chloral and Aluminium Chloride.—When alcohol and chloral are brought together the temperature rises, and as is already known, a liquid is formed which may be easily identified as trichloroacetal.   As we were especially interested in the chloral reactions which take place in the presence of aluminium chloride, the following experiment was tried: Seventy grams of absolute alcohol were placed in a flask and cooled down to below zero by ice-water and ammonium nitrate; 100 g. of chloral and 25 g. of aluminium chloride were quickly added and vigorously shaken. A turbid mass indicated that the reaction which had taken place was the same as that which takes place with alcohol and chloral alone.   However, when the chloride was added under ordinary conditions, the temperature rose and hydrochloric acid was liberated.   By adding 70 g. more of the chloride and allowing to stand for 48 hours, the reaction appeared to have entirely changed.   The mass thus treated was poured into ice-water and the insoluble part and extracted with ether.   The extract was dried with calcium chloride, the ether evaporated off and the residue subjected to fractional distillation.   A small part passed over below the boiling point of ether.   It had a sharp pungent odor.   The second distillate was easily recognized as common acetaldehyde.   Then some ether passed over and, at about 100°, chloral hydrate.   After the above substances had been removed, the temperature rapidly rose to 170–200°, when a distinctly aromatic oil distilled over.   After redistillation, it boiled at 197°.   It had the general physical properties of trichloroacetal.

The appreciable quantity of acetaldehyde would indicate that chloral acts as an oxidizing agent.

We were somewhat surprised to find that the trichloroacetal formed in this reaction did not possess all of the properties generally ascribed to it. It may be of interest here to note that an isomer of trichloroacetal was obtained by Liebens.[1] It is not impossible that the above substance is the one which Liebens describes.

Benzyl Alcohol, Chloral and Aluminium Chloride.—The reaction between benzyl alcohol and chloral is less energetic than between common alcohol and chloral; so much so, in fact, that the reaction may be brought about at the ordinary room temperature. The reaction was brought about as follows: 75 g. of benzyl alcohol, 50 g. of chloral and 45 of aluminium chloride were brought together at room temperature. The action began immediately. Hydrochloric acid was liberated and the whole mass changed to a chocolate-brown color. The mass was allowed to stand for 24 hours and then treated with water in order to remove the unchanged chloral and the aluminium chloride. The residue was then distilled with steam. That which passed over was extracted with ether, the latter removed and the extracted substance subjected to distillation. Most of it passed over at 173° and was identified as benzaldehyde. It would appear, therefore, that chloral in this particular case acts as an oxidizing reagent, changing the benzyl alcohol to the aldehyde.

The mass which remained in the flask was extracted with ether, the ethereal solution washed with water, dried, and the ether removed by evaporation; the residue was then subjected to distillation. It distilled over at from 150–300°, thus indicating by the variable boiling point that the substance is a mixture of two or more compounds. It is a liquid at the ordinary temperature. It proved to be organic, but it contained a large amount of chlorine. It also gave the aldehyde reaction. In order to obtain it in a pure enough form for analysis it was again subjected to distillation. Unfortunately, we were unable to obtain a substance with a constant boiling point. As this substance is of considerable interest it has been set aside for further investigation as soon as time will permit.

Phenol, Chloral and Aluminium Chloride.—Forty-nine grams of phenol, 40 g. chloral and 35 g. of aluminium chloride were brought together under conditions already mentioned, and allowed to stand for two days at freezing temperature. Hydrochloric acid gas was liberated in large quantities. The whole mass was then treated with water and finally distilled with steam. That which was left in the distilling flask was a reddish brown, waxy mass with a distinct phenol odor. The waxy substance was thoroughly washed with water. The odor of phenol slowly disappeared and the substance changed to a semisolid. The substance thus purified

[1] *Ann.*, 104, 114 (1857).

was quite soluble in alcohol and ether, from which it refused to crystallize. Benzene dissolved a part readily, while a part was quite insoluble. The insoluble part appeared as a fine crystalline powder. The substance was filtered off, washed with benzene, was finally recrystallized from acetic acid, in which it is very soluble. Thus purified, the substance melted at 212° and analyses gave numbers which correspond to p-dihydroxydiphenyltrichloroethane, which was obtained by ter Meer[1] by treating chloral and phenol with concentrated sulfuric acid. To prove the constitution, however, the compound was converted into an acetyl derivative which had a m. p. of 138°—the same which ter Meer found for the substance obtained from sulfuric acid. The part which was soluble in benzene is a dark brown, resinous powder which contains chlorine. This substance is new and is now being studied.

Diresorcyldichloroethylene.—Resorcin and chloral, when brought together, do not combine with each other, but the chloral is absorbed by the solid resorcin forming a solid mass. The substances were therefore first dissolved in carbon disulfide before adding the chloride. Twenty-five grams of resorcin and 20 g. of chloral were dissolved in 200 g. of carbon disulfide and 20 g. of aluminium chloride cautiously added. The condensation product was purified by treating with water and steam and finally from alcohol and acetic acid. The substance thus purified was a brown powder with an unpleasant odor. It contained a considerable quantity of aluminium. It attacked the eyes vigorously. As results were not very satisfactory the three substances were brought together in different proportions. Twenty grams of resorcin, 40 g. of chloral and 15 g. of aluminium chloride were brought together as indicated above. After thoroughly purifying, the substance appeared as a light brown powder without odor. It contained some inorganic matter, presumably aluminium chloride. It was purified by dissolving in alcohol and reprecipitated with dilute hydrochloric acid. By repeating this process several times the powder was obtained practically free from aluminium.

Analysis gave: C = 53.63, H = 3.30, Cl = 22.77. Calc. for $CCl_3(C_6H_3(OH)_2)_2$: C = 53.83, H = 3.21, Cl = 22.44.

Tetraacetyldiresorcyldichloroethylene.—In order to determine the number of hydroxyl groups in the above resorcyl derivative it was treated with acetic anhydride and the substance thus formed purified and analyzed. Five grams of the resorcyl compound, 5 g. of dry sodium acetate and 25 g. of acetic anhydride were heated to boiling for three hours. The excess of anhydride was changed to the ester with alcohol and ester distilled off. The light brown powder was left, which, on examination, appeared to be the pure acetic ester.

Analysis gave· Cl = 14.70. Calc.: Cl = 14.57.

[1] *Ber*, **7**, 1200 (1874).

Anisol Chloral and Aluminium Chloride.—Dianisyltrichloroethane was prepared in the following manner: 100 g. of anisol (2 mol), 80 g. of chloral (1½ mol) were brought together and cooled to 0°. Twelve grams of aluminium chloride were added in small portions and with frequent shaking. The mass became thick and changed to a dark green color. It was kept at a freezing temperature for 24 hrs. After the excess of chloral and aluminium chloride had been removed by means of warm water, the substance was purified, first by steam distillation and finally by crystallization from hot alcohol. After recrystallizing several times the substance appeared as thick, shiny, transparent crystals. They were soluble in nearly all of the common organic solvents and had a melting point of 78°.

Analyses checked for the formula, $(CH_3OC_6H_4)_2 = CHCCl_3$.

Elbs is supposed to have prepared this substance by condensation of anisol and chloral hydrate by means of concentrated sulfuric acid. The Elbs substance, appeared at first to be a different compound from the one given above, inasmuch as he gave the m. p. as 92°. In order to determine whether or not the two substances are really the same, Elbs' experiment was repeated. As a result crystals were obtained which were identical with those obtained with aluminium chloride. The crystals did not have the m. p. 92°, as given by Elbs, but 78°, the same as the compound obtained with aluminium chloride.

In order to study the constitution of dianisyltrichloroethane more fully, it was reduced by means of zinc. Ten grams of the compound were placed in a flask connected with a reflux condenser with 100 cc. of alcohol. Ten grams of zinc dust, together with strong alcoholic ammonia, were added and the whole mass heated on a water bath for sixteen hrs. The insoluble substance was then filtered off and the filtrate allowed to stand when fine needle-shaped crystals separated out with a melting point of 212°, the same that Kopp[1] and Weichell[2] obtained for *p*-dimethoxystilbene.

Dianisyldichloroethylene.—This substance was obtained by treating dianisyltrichloroethane prepared from anisol, chloral and aluminium chloride with alcoholic potash. The experiment was carried out as follows: 15 g. of the anisyl compound were placed in a flask and heated with alcoholic potash on a water bath connected with a reflux condenser for 12 hours. At the end of that time the alcohol was evaporated off and the inorganic substance removed by warm water in a separatory funnel. The dianisyldichloroethylene was then dried and recrystallized from hot alcohol. The m. p. was 109°.

Analysis gave the following: Cl = 22.58. Calc., 22.72.

[1] *Ber.*, 25, 603 (1892).
[2] *Ann.*, 279, 341 (1894)

Octonitrodianisyltrichloroethane.—The octonitro compound was easily prepared by treating the dianisyltrichloroethane with fuming nitric acid. Five grams of dianisyltrichloroethane were brought in contact with 50 cc. of fuming nitric acid after first being cooled down to $0°$. The acid was added slowly and the whole allowed to stand over night. The whole mass was then poured into water when the nitro compound separated out. It was purified by crystallizing from alcohol. The substance thus obtained was a beautiful light yellow, felt-like mass of crystals. The m. p. was $173°$.

Analysis gave the following. N = 15 89. Calc., 15.95.

Phenetol, Chloral and Aluminium Chloride.—Chloral reacts with phenetol in the presence of aluminium chloride, forming analogous compounds to those already described with anisol.

Diphenetyltrichloroethane.—Fifty grams of phenetol, 50 of chloral and 10 of aluminium chloride were treated according to the general method already described. After the reaction was completed the compound was removed, excess of the reagents removed by means of water and finally recrystallized. The substance obtained proved to be colorless, hexagonal crystals with a sharp m. p. of $105°$.

Analysis of the dried substance gave the following:

Found: C = 57.4, 57 55; H = 5 33, 4 60; Cl = 28 59, 28 44.   Calc.: C = 57.95; H = 5 09; Cl = 28.42.

As the substance proved to be of unusual interest, we undertook to prepare it by using concentrated sulfuric acid, assuming that we should find, in this case, exactly what we found in the case of anisol, that the same identical substance is formed whether the reaction is brought about with aluminium chloride or concentrated sulfuric acid as a condensation re-agent. We obtained with sulfuric acid beautiful transparent crystals which, after crystallizing from alcohol, melted at $104°$, the same as the compound prepared from aluminium chloride.

Diphenetyldichloroethylene.—This compound may be easily prepared by heating diphenetyltrichloroethane with alcoholic potash. The dichloro compound was purified from hot alcohol. It crystallizes in fine needles and melts at $97°$. The crystals are soluble in all the common organic solvents.

Analysis gave the following: Cl = 20.96.   Calc . Cl = 20 84.

p-Diethoxystilben.—This compound was prepared by reduction of the diphenetyldichloroethylene with zinc dust and alcohol and ammonia. The compound crystallizes in fine needles. It is moderately soluble in benzene but with difficulty in all other organic solvents; m. p. $207°$. It is identical with the compound prepared from diphenetyldichloroethylene which Wichel prepared by an entirely different method.

Octonitrodiphenetyltrichloroethane.—Five grams of diphenetyltrichloro-

ethane were treated with 60 cc. of fuming nitric acid at freezing tempera-
ture for 16 hrs., at which time the reaction seemed to be complete. The
mass was then poured into water, the precipitation removed by filtration,
washed and recrystallized from hot alcohol. The substance consisted of
fine yellowish needles which melt at 137°.

Found: C = 29.42, H = 1.65, N = 15.86.   Calc.: C = 29 47, H = 1.50, N =
15.28.

Diphenetyltribromoethane.—Fifty grams of phenetol (2 mol) and 57 g.
(1 mol) of bromal were brought together in a liter flask and cooled down
to 0°.   Ten grams of aluminium chloride were slowly added and the mixture
vigorously shaken after the addition of each portion of chloride.   It
changed to a dark green syrupy liquid.   After standing 24 hrs. in ice-
water the whole mass was purified by washing with warm water and finally
with steam.   The partially purified mass was then crystallized out of hot
alcohol in yellowish crystals with a m. p. of 112°.

Analysis of the dried substance gave the following:

Found: C = 42 89, H = 3.81, Br = 47 41.   Calc C = 42.60, H = 3.75, Br =
47.33.

Octonitrodiphenetyltribromoethane.—Eight grams of diphenetyltribromo-
ethane were cooled down to 0° and 60 cc. of fuming nitric acid very slowly
added.   After standing in the freezing mixture for 20 hrs., the whole mass
was poured into ice-water, the precipitate removed, washed and crys-
tallized from hot alcohol as yellow crystals, with a sharp melting point
of 153°.   The substance proved to be analogous in every way to the octo-
nitrodiphenetyltrichloroethane.

Found: N = 13.08.   Calc.: N = 12.92.

As the above-mentioned nitro compounds were easily obtained in
such remarkably pure form, they were at first supposed to be analogous
with those prepared, studied and analyzed by Elbs.[1]   A careful examina-
tion shows, however, that they are entirely different from those described
by Elbs.   We were somewhat surprised to find that nitric acid, like
hydrochloric, does not hydrolyze the ester so along as the temperature
is kept near 0°.   On the contrary, strong nitric acid gave almost quanti-
tative nitro products, both with the chloride and bromide of phenetol.

Aluminium bromide was tried with phenetol and bromal.   We were
surprised to find that no reaction took place in the presence of the bro-
mide, although a vigorous reaction took place when aluminium chloride
was substituted for the bromide.   Aluminium bromide, therefore, does
not act as a catalyst in this case, either in the ordinary sense of the term,
breaking off hydrobromic acid, or as a condensation reagent.

Phenylether Chloral and Aluminium Chloride.—As has already been
shown, the mixed aromatic-aliphatic ethers are readily condensed with

[1] *J. prakt. Chem.*, 47, 62 (1893).

chloral in the presence of aluminium chloride, but the phenols themselves are not acted upon at all in the cold, and slowly when warmed. It was therefore of some little importance to determine whether phenylether, or diphenyloxide, really possessed the same properties as the mixed ethers to which anisol and phenetol belong. Experiments were carried out in a similar manner to those with mixed ethers, using the following proportions: 34 g. (1 mol) of the ether, 30 g. (1 mol) of chloral and 30 g. (1¹/₄ mol) aluminium chloride. After allowing to stand for some time, the whole was treated with water and finally distilled with steam. The residue was extracted with ether. A part only was found to be soluble. The soluble substance, after ether had been removed, was a thick liquid which finally appeared as a yellowish resin. It contained aluminium and chlorine. It did not give the aldehyde reaction. Owing to the readiness with which it decomposed, it was not obtained in pure enough form for analysis.

The part which proved to be insoluble in ether was treated with benzene. A part dissolved. The benzene soluble part, after evaporating the benzene, appeared as a yellowish amorphous powder which likewise contained aluminium. Analyses of the substance were not satisfactory, probably on account of the fact that the powder could not be obtained in a perfectly pure form. The above experiment was repeated, using different proportions of substances, but each time with the same results.

Condensation of Ketones with Chloral Hydrate by means of Aluminium Chloride.

Acetophenone, Chloralhydrate and Aluminium Chloride.—Chloralhydrate combines with acetophenone by means of aluminium chloride even in the cold. The substance formed seems to be complex, containing a small quantity of aluminium which could not be removed. Best results were obtained by using 25 g. (2 mol) of acetophenone, 16 g. (1 mol) of chloralhydrate, with 15 g. of aluminium chloride, and warming under the same conditions as indicated in previous experiments. The product obtained was a thick, yellowish oil which finally changed to a solid, resinous mass. It proved to be soluble in all the common solvents. Vacuum distillation gave a distillate at 170° and 40 mm. It appeared to be the result of decomposition.

Benzophenone, Chloralhydrate and Aluminium Chloride.—While chloral combines readily with acetophenone, it apparently does not combine at all with benzophenone, for after treating with chloral in the presence of aluminium chloride, no reaction took place, as is shown by complete recovery of the original ingredients.

Condensation of Acids with Chloral and Aluminium Chloride.—Chloralaluminium-monochloroacetate, $Al_2Cl(OOCCH_2)_3CCl_3CHO$. Contrary to

expectations chloral combines with acetic acid or other monobasic acids. The first experiment was as follows: 20 g. of acetic acid, 25 g. of chloral and 20 g. of aluminium chloride were brought together at ordinary room temperature. A reaction began immediately and the aluminium chloride passed into solution with liberation of hydrochloric acid. At the same time a yellow, pasty mass was formed. This yellow paste was first treated with water, the whole mass dissolved, and on evaporating the yellowish solid substance was again obtained. An attempt was made to distil it *in vacuo*, but it decomposed even at 15 mm. pressure. The experiment was therefore repeated, but instead of treating with water dry ether was used. The greater part proved to be insoluble. The impurities, however, were insoluble. Ether was used, therefore, in removing the impurities. After treating several times with dry ether the residue was dried in the vacuum desiccator. The substance thus purified proved to be insoluble in most of the organic compounds. It dissolved with difficulty, however, in absolute alcohol; it was insoluble in cold water but quite soluble in hot.

The compound possesses a distinct odor of chloral together with a distinct aromatic odor. It is a light yellow powder which decomposes before reaching the melting point. It readily burns on platinum foil, leaving aluminium oxide. The salt, after repeated washings with dry ether, was subjected to analysis with the following results:

Found: Cl = 26.44 and 26.39, Al_2O_3 = 10 32. Calc.: Cl = 26 55, Al = 10 17.

In order to distinguish between the chlorine in the group $Al_2Cl(OOCCH_3)_5$ and the chlorine in the chloral the whole was treated with nitric acid and silver nitrate, with the hope that the silver nitrate would remove the chlorine from the aluminium group only. We found, on the contrary, that the chlorine in the chloral was also removed, and other methods of separation were tried.

It was found that when the powder was treated with cold absolute alcohol the chloral was completely removed while the aluminium radical remained undissolved.

The salt was therefore treated with absolute alcohol until all of the chloral had been removed. The residue was then treated with water until all of the aluminium had been removed. The residue when tested showed the presence of chlorine while the alcohol was found to contain all of the chloral.

Determinations of chlorine in the alcoholic and aqueous solutions showed that just three-quarters of the total amount of chlorine in the substance had been extracted by the alcohol, the balance being left in the aqueous solution. These results indicate that a quantitative separation of the chloral from the aluminium chloroacetate had been made and that the above formula is therefore correct.

Very recently Böeseken and Cluwen[1] succeeded in isolating a compound formed from aluminium chloride and acetic anhydride, the reaction which they represent as follows:

$$2(CH_3CO)_2O + AlCl_3 = AlCl(OCOCH_3)_2 + 2CH_3COCl.$$

They also found that the above compound formed a double salt with ethylether, $(CH_3CH_2)_2O.2AlCl(OCOCH_3)_2$.

Benzoic Acid, Chloral and Aluminium Chloride.—Benzoic acid does not react with chloral. Several experiments were tried with the acid in solution and finally with chloral itself in the presence of aluminium chloride, but with little or no change. The solution turned brown, but on treating with water, pure benzoic acid was recovered.

Pyridine, Chloral and Aluminium Chloride.—When chloral, pyridine and aluminium chloride are brought together a vigorous reaction takes place, and there is formed a substance which has the appearance of common butter. It was found to be insoluble in practically all of the organic solvents. As this substance could not be obtained in pure form the experiment was modified by bringing the chloral and aluminium chloride together and afterward adding the pyridine. The mass became hot from the heat of reaction and a white vapor was given off, but no hydrochloric acid was liberated.

After the whole mass had been treated with water a bright yellow powder was separated out which proved to be insoluble in practically all the solvents. It contained both aluminium and chlorine and had the odor of pyridine. The substance appears to be a single substance, but, up to the present time, no solvent has been found for it. It will be more exhaustively studied in the near future.

Summary.

As will be seen, from the above general survey, practically all of the organic groups of compounds which have been treated with chloral, chloral hydrate and bromal in the presence of aluminium chloride at low temperatures, have formed distinct condensation products. The treatment of organic compounds with chloral and aluminium chloride at low temperatures, therefore, offers an important means of organic condensation, as some of the compounds prepared and described in this paper cannot be obtained by the Baeyer or sulfuric acid reaction.

No single group of compounds has been exhaustively studied, inasmuch as the important fact to be determined in this preliminary work was, first, whether or not aluminium chloride can be used as a condensation reagent; and second, whether or not it acts catalytically.

The evidence presented in the above experiments, we believe quite sufficient proof that aluminium chloride acts as a catalyst, at the same time, however, playing the part of a simple dehydrating reagent.

[1] *Rec. trav. chim.*, **31**, 369 (1912).

That temperature plays a most important part in this reaction is evident from the results of all the experiments made thus far. In every case it was found that rise in temperature, even but a few degrees above zero, materially changed the reaction and increased the decomposition of both the reacting components. In some cases, as in the ethers, a slight rise above zero not only causes saponification of the ether but also complete decomposition.

In exceptional cases, the chloride seems to act simply as a dehydrating reagent and therefore not as a catalyst in the ordinary use of the term. In most cases, however, it unquestionably plays the part of the catalytic agent, notwithstanding the fact that when equilibrium is finally reached a part of the chloride at least has been converted into the oxide or the hydroxide.

It is evident, from the wide range through which aluminium chloride reacts in the presence of chloral, that the final or complete equilibrium embraces several separate and distinct chemical changes. Some of these are purely catalytic while others apparently are not, although they are entirely dependent upon the catalytic part of the reactions. If we assume, for instance, that aluminium chloride reacts purely as a catalyst, as is evidenced in some of the above experiments, then the equation would be represented as follows:

$$6R.H + 3CCl_3CHO + Al_2Cl_6 = 3CCl_3CHR_2 + Al_2Cl_6 + 3H_2O$$

This perfectly normal equation, however, by no means excludes other reactions before final equilibrium is reached, for we have not only shown that another reaction takes place before the one indicated above, forming an aluminium alkyl exactly as in the case of Friedel-Crafts reaction, but in a few cases these alkyls were isolated, as will be shown in the second paper now well under way.

From the evidence already presented, a series of reactions may be given as representing the chemical changes which actually take place when equilibrium is finally reached. In the first part of the reaction, aluminium chloride doubtless acts as a pure catalyst as may be indicated by the following equation·

$$C_6H_6 + Al_2Cl_6 = Al_2Cl_5-C_6H_6 + HCl, .$$

or

$$6C_6H_6 + Al_2Cl_6 = Al_2(C_6H_5)_6 + 6HCl$$

Then through catalytic action of the hydrogen ions of the hydrochloric acid, the second part of the reaction takes place:

$$Al_2(C_6H_5)_6 + 3CCl_3CHO + 6HCl = 3CCl_3CH(C_6H_5)_2 + Al_2Cl_6 + 3H_2O,$$

or

$$Al_2(C_6H_5)_6 + 3CCl_3CHO + 6HCl = 3CCl_3CH(C_6H_5)_2 + Al_2O_3 + 6HCl$$
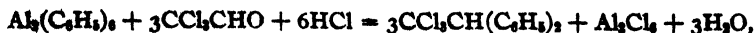
Either or both of these reactions may take place inasmuch as water, hydrochloric acid and, in a few cases, aluminium oxide are liberated.

Detailed work along several lines mentioned above is now under way. So far as the work has progressed, aluminium chloride in each case unquestionably plays the part of a catalyst, whether hydrochloric acid, water, aluminium hydroxide or aluminium oxide is formed during the reaction.

THE UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN

THE ACTION OF TRIOXYMETHYLENE ON THE VARIOUS HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY GEO B FRANKFORTER AND V. R KOKATNUR.
Received May 13, 1914.

Ever since Friedel and Crafts discovered the reaction which bears their names, chemists have used it in various ways in order to bring about certain chemical changes, in some cases under entirely different conditions from those recorded by the authors themselves. Thus, Scholl and Seer[1] showed that anhydrous aluminium chloride, in a few cases, actually breaks off free hydrogen instead of hydrochloric acid. Recently Page[2] has shown that aluminium chloride possesses the power of transporting chlorine to certain organic compounds. Finally it has been found, under proper physical conditions, to act as a dehydrating agent like concentrated sulfuric acid. It has been shown by Kritchevsky and one of us that when an aldehyde, as chloral, and a hydrocarbon, either benzene or one of its homologs, are brought together in the presence of aluminium chloride at 0°, a reaction analogous to the Baeyer reaction takes place.

In order that the last reaction mentioned might be more thoroughly studied, experiments similar to those mentioned above with benzene and chloral were begun, using trioxymethylene, however, instead of chloral. In each case the same general condensation reaction took place. In a few cases, the reaction seemed to be comparatively simple, while in others it appeared to be extremely complex. This variation seemed to be influenced, largely, by temperature, as a result of the way in which the aluminium chloride was added, either fast or slow, or as to whether the whole mass was kept in a freezing mixture during the reaction. Finally, it was hoped that, in addition to studying the reaction itself, some light might be thrown on the constitution of trioxymethylene.

The molecular structure of trioxymethylene is generally considered to be a ring compound, in which the oxygen and the methylene groups are

[1] *Monatsh.*, 33, 1 (1912).
[2] *Ann.*, 225, 196 (1884).

symmetrically arranged. In case the accepted theory is a fact, we hoped to prepare condensation products by breaking the ring and substituting hydrocarbon radicals for one, or more, of the oxygen atoms, as indicated by the following formulas:

$$CH_3\!\!\left\langle\!\begin{array}{l} O\text{---}CH_2\text{---}R \\ O\text{---}CH_2\text{---}R \end{array}\right. \qquad O\!\!\left\langle\!\begin{array}{l} CH_2\text{---}R \\ CH_2\text{---}R \end{array}\right. \quad \text{and} \quad CH_3\!\!\left\langle\!\begin{array}{l} R \\ R \end{array}\right.$$
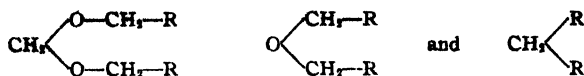
where R represents either benzene or one of its homologs.

On going over the literature of trioxymethylene, it was found that Grassi and Masselli[1] had prepared compounds analogous to those which we had hoped to prepare by breaking the ring and substituting inorganic radicals for the oxygen. Thus by treating trioxymethylene with acetic acid and water, they obtained trioxymethylene hydrate,

$$CH_3\!\!\left\langle\!\begin{array}{l} O\text{---}CH_2\text{---}OH \\ O\text{---}CH_2\text{---}OH \end{array}\right.$$
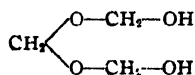
Then, by treating the hydrate with hydrochloric acid, the trioxymethylene chloride was formed. And finally, by treating the chloride with benzene, they obtained diphenylmethane. They assumed that the hydrochloric acid broke the ring compound down into formaldehyde, at the same time forming a hydrochloride, $ClCH_2OH$. This compound then reacted with the benzene, forming diphenylmethane. They failed to prepare any of the oxy compounds.

As has already been stated, the reaction between trioxymethylene and the hydrocarbons varies widely, depending upon the conditions under which the reaction takes place. Under none of these conditions, however, were we able to prepare any of the oxy compounds, although various complex hydrocarbons were prepared, as will be shown later. Notwithstanding the fact that no oxy compounds could be isolated, the truth remains that trioxymethylene acts differently from formaldehyde in the presence of aluminium chloride. This fact may mean that some of the oxy compounds are actually formed in the reaction and are broken down into the various hydrocarbons before equilibrium is finally reached.

Trioxymethylene has never before been used with aluminium chloride, consequently no condensation products have ever been made; neither has it been studied in connection with concentrated sulfuric acid. As a matter of fact, formaldehyde itself has never been studied in this connection. It has been used, however, with concentrated sulfuric acid, yielding compounds which, in many cases, are the same as those obtained with trioxymethylene and aluminium chloride.

[1] *Gas.*, **28**, 477 (1898)

Experimental Part.

Benzene and Trioxymethylene.—To 500 cc. of benzene were added 35 g. of trioxymethylene, the mixture cooled to 0° and 170 g. of anhydrous aluminium chloride added piecemeal. An automatic stirrer was used and the mixture was stirred continuously while the aluminium chloride was being added. The temperature was never more than 20°, though most of the time it was less than 10°.

After about 50 g. of aluminium chloride had been added, the color of the mixture changed to a reddish brown and copious fumes of hydrochloric acid were liberated. The stirring was continued for some time after all aluminium chloride had been added. It required 10 hrs. to complete the reaction. During this time, hydrochloric acid continued to pass off. After the reaction had apparently ceased, the whole mixture was placed in a refrigerator for three or four days. At the end of that time it was removed and ice-water added, in order to decompose all aluminium chloride without rise in temperature. After a sufficient quantity of water had been added an oily substance separated out and floated on the water. Some solid substance remained at the bottom of the flask. There was also some solid material which was lighter than water but heavier than the oil. This separated out and remained on the surface of water just below the oily layer. The whole was then extracted with ether. All, except the solid substance on the bottom of the flask, dissolved. The ether solution was then separated from the water and the insoluble substance, which was set aside for further treatment.

The ether extract was subjected to fractional distillation and the distillates were collected separately, as follows: (*a*) between 40°-80°, (*b*) 80°-130°, (*c*) 250°-280° and (*d*) 280°-360°. A preliminary examination showed that distillate (*a*) was largely ether with some benzene. Distillate (*b*) was found to contain largely benzene with small amounts of toluene. From 130° the temperature rapidly rose to 250° and an aromatic liquid continued to distil over until a temperature of 280° was reached. Then a white substance of somewhat waxy nature passed over and solidified on the walls of the condenser. This substance continued to distil over until the temperature had reached 360°. Distillation was then stopped as the tarry, resinous solid material remaining in the flask showed signs of decomposition. A peculiar blue fluorescence was observed in the distillate. The resinous material was set apart for further treatment.

As the yield of products was not entirely satisfactory, the above experiment was repeated, varying the temperature and the proportion of trioxymethylene. In each case the same products were obtained, although the yield of the liquid and solid distillates (*c*) and (*d*) varied. In the above experiment the quantity of liquid distillate (*c*) was small. When 40 g. of trioxymethylene were used under exactly the same conditions, the yield

of both (c) and (d) was greater, and when 50 g. were used there was a still larger yield of both the liquid and the solid distillates (c) and (d). On the contrary, when 100 g. of trioxymethylene were used, there was a good yield of the liquid distillate (c) and no yield of the solid (d). Even when the temperature was allowed to rise to 40°–50° the same products were formed, although the yield varied.

The liquid distillate (c) was redistilled, after which it showed signs of crystallization. The redistilled oil was therefore cooled in a freezing mixture, when it crystallized in colorless prismatic needles. The m. p. of the substance was found to be 26°–27°. It was at once suspected to be diphenylmethane. Hence it was compared with Kahlbaum's diphenylmethane in appearance, boiling point and other characteristics. Kahlbaum's diphenylmethane, although marked "C. P.," was found to be impure. It was a yellowish colored liquid. It began to distil at 254° and continued to 261°. After distillation, however, it was colorless and at once crystallized in colorless, prismatic needles, m. p. 26°–27°.

Our diphenylmethane distilled over between 259° and 262°. It was perfectly colorless and crystallized in colorless prismatic needles. The various tests indicated that it was diphenylmethane. It also showed the characteristic blue fluorescence. Baeyer[1] first obtained diphenylmethane by treating benzene with formaldehyde in the presence of sulfuric acid; and later Nastukoff,[2] on repeating Baeyer's experiments, showed that phenylformol was formed, and this substance, by dry distillation, yielded not only diphenylmethane but also toluene xylene and anthracene.

The solid distillate (d) which passed over between 280°–360° was finally dissolved in a mixture of hot benzene containing a little alcohol, as this mixture was found to give best results. On cooling the solution, a leafy, white substance crystallized out. This was filtered off, washed with alcohol several times to remove the last traces of diphenylmethane and recrystallized three or four times. The pure crystals thus obtained were dried and the melting point was found to be 210°–211°. The crystals were monoclinic plates of pearly luster. The crystals both in solution and out of it showed a beautiful fluorescence. Analysis gave numbers for anthracene, although the melting point was a little low. It gave all the reactions for anthracene and on oxidation gave anthraquinone, leaving no doubt as to its identity. The yield of both diphenylmethane and anthracene was exceptionally good.

The fact that diphenylmethane and anthracene are the two principal compounds formed in the reaction throws some light on the nature of the reaction. From the amounts of these two compounds obtained, it is

[1] *Ber.*, **5**, 1099 (1872).
[2] *J. Russ. Phys. Chem. Soc.*, **35**, 825 (1903).

evident that equal molecular quantities are formed. In view of this fact, the equation may be represented as follows:

$$4C_6H_6 + (CH_2O)_3 + AlCl_3 = CH_2(C_6H_5)_2 + C_{14}H_{10} + 3H_2O + AlCl_3 + H_2$$

As equal molecular quantities of diphenylmethane and anthracene are formed in this reaction, we were at first led to believe that the trioxymethylene molecule is not symmetrical, the methylene group forming the diphenylmethane having different molecular nature from the other two groups in the molecule. On the contrary, Baeyer obtained diphenylmethane from benzene and formaldehyde by means of sulfuric acid; and Nastukoff by the same reaction obtained both diphenylmethane and anthracene. These facts scarcely permit such a conclusion, although the reaction is none the less interesting.

Baeyer[1] showed that, when diphenylmethane was further treated with formaldehyde and sulfuric acid, condensation occurred, forming dihydroanthracene. In order to determine whether or not trioxymethylene would act the same as formaldehyde, 50 g. of diphenylmethane and 9 g. of trioxymethylene were treated with 20 g. of aluminium chloride, according to the method already given. On examining the products after the reaction had been completed a considerable quantity of diphenylmethane was recovered. There was left in the flask, after distilling off the diphenylmethane, a tarry mass which does not contain anthracene. This was set aside for examination later. Therefore, trioxymethylene does not act in the presence of aluminium chloride like formaldehyde in the presence of sulfuric acid.

In order to show whether or not trioxymethylene forms the same compound with the benzene homologs in the presence of aluminium chloride which formaldehyde does in the presence of sulfuric acid, a series of experiments was made, using toluene, xylene and mesitylene instead of benzene.

Toluene and Trioxymethylene.—Fifty grams of trioxymethylene were dissolved in 400 cc. of toluene and 100 g. of aluminium chloride added piecemeal. A large amount of heat was liberated, but the temperature was not allowed to go above 65°. The whole mass changed to a reddish brown color and fumes of hydrochloric acid were given off. The upper layer showed a deep blue fluorescence. The whole mass was kept in a cool place for four days, and after adding ice-water, subjected to the same process described under benzene. Distillate (a) passed over between 50° and 120°, (b) between 290° and 310°, and (c) between 310° and 400°. After the small quantity of (a), which on examination was found to be a mixture of ether, toluene and benzene, had passed over, the temperature immediately rose to 290°. At this point oil began to distil over and con-

[1] *Ber.,* 6, 222 (1873).

tinued until a temperature of 310° was reached. The distillate then began to solidify on the walls of the condenser. The solid continued to pass over until a temperature of 400° was reached. Owing to decomposition the distillation was stopped. A dark, resinous substance remained in the flask. This material was reserved for further investigation.

On redistilling the oil which was collected between 290°–310°, most of it passed over between 285–7°. It showed a brilliant blue fluorescence. It was further purified and analyzed. Analysis and physical and chemical properties checked well for ditoluylmethane.

The semisolid substance which came over between 310°–400° was then dissolved in a mixture of alcohol and benzene, from which it was obtained in a well crystallized form. It was recrystallized several times by this means, when the constant m. p. of 225°–226° indicated that it was pure. Analysis and general properties checked well for dimethylanthracene, a compound prepared by Friedel and Crafts[1] by treating toluene and methylene dichloride with aluminium chloride. As this reaction is evidently an exact duplicate of the reaction with benzene, it may be represented as follows:

$$4C_6H_5CH_3 + (CH_2O)_3 = CH_2(C_6H_4CH_3)_2 + C_{16}H_{15} + 3H_2O + H_2$$

It is also interesting to note that Anschütz[2] obtained the same dimethylanthracene by treating toluene with acetylene tetrabromide and aluminium chloride.

Xylene and Trioxymethylene.—To a mixture of 500 g. of o-xylene, b. p. 142°, and 50 g. of trioxymethylene, 100 g. of aluminium chloride were added, with constant stirring. The temperature rose to 65° and copious fumes of hydrochloric acid were liberated. The mass seemed to divide into two layers; the upper one showing a deep greenish blue fluorescence; the lower one was dark brown. The whole was allowed to stand at ordinary room temperature for three days, at the end of which time the reaction seemed to be complete. The whole mass was treated with ice-water, allowed to stand for some time and finally extracted with ether. The extract was drawn off, the ether removed and the residue distilled at ordinary pressure. The distillates were collected as follows: (*a*) between 70° and 150°, (*b*) 200° and 330°, and (*c*) between 330° and 400°. After these distillates had been removed there remained in the flask a tarry substance. After removing distillate (*b*) an air condenser was used and the solid distillates were thus easily collected for further examination. The first distillate (*a*) consisted of a mixture of hydrocarbons, benzene, xylene, and possibly some toluene. Distillate (*b*) was redistilled, when a large part passed over between 311°–313°. It was wonderfully fluorescent, more so even than diphenylmethane and ditoluylmethane. Analysis of

[1] *Ann. chim. phys.*, [6] 11, 266 (1887).
[2] *Ann.*, 235, 172 (1886).

the purified substance gave numbers for $C_{17}H_{20}$ or dixylylmethane. This compound has evidently never before been made, although a substance of the same empirical formula,[1] a duryl benzyl compound, has been prepared.

Tetramethylanthracene.—Distillate (c), or that which passed over between 330°–400°, was now examined. It was semi-solid, evidently composed of two or more compounds, and was purified by washing with chloroform. This rapidly took out the oily substance, leaving behind most of the solid substance. The latter was then recrystallized from a mixture of benzene and alcohol. By repeating the process several times the substance was obtained in pure form. It crystallized in yellow monoclinic plates of pearly luster. In solution it possessed an intense green fluorescence. It does not appear to have a melting point but decomposes at 233°–235°. It can be sublimed, however, without difficulty, forming crystals with wonderful iridescence.

Found: C = 92 23 and H 7 22. Calc. for $C_{18}H_{18}$: C = 93.3, H = 7.7.

Friedel and Crafts[2] prepared a tetramethylanthracene from *m*-xylene with a m. p. of 162°–163°, while Anschütz[2] obtained from *m*-xylene an entirely different tetramethylanthracene with a m. p. of above 280°. Dewar and Jones[4] obtained the same compound described by Anschütz which they designated as 2 : 4 : 6 : 8 derivative. Anschütz also obtained from *o*-xylene a tetramethyl compound with a m. p. of 280°, almost the same as the meta compound. It is evident that the one prepared above is an isomeric form, the exact structure of which has not yet been obtained. From what has already been stated concerning these reactions, this one may be represented as analogous to those already given:

$$4C_6H_4(CH_3)_2 + (CH_2O)_3 =$$

$$CH_3 \diagdown \begin{matrix} C_6H_3(CH_3)_2 \\ \\ C_6H_3(CH_3)_2 \end{matrix} + (CH_3)_2C_6H_2 \diagdown \begin{matrix} CH \\ \\ CH \end{matrix} \diagup C_6H_2(CH_3)_2 + H_2 + 3H_2O$$
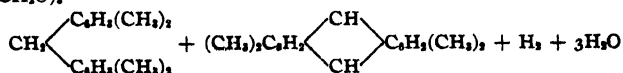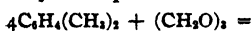
Mesitylene and Trioxymethylene.—Two hundred grams of mesitylene were brought together with 30 g. of trioxymethylene at ordinary temperature and 55 g. of aluminium chloride added with constant, vigorous stirring. The temperature rose to 50°, hydrochloric acid gas was libera-. and the color changed to a dark red. Two layers again appeared, the upper one having a deep violet fluorescence. After allowing it to stand for two days at ordinary room temperature, water was added, and finally the whole mass was extracted with ether. The addition of ether precipitated an amorphous substance which was at first thought to be an aluminium compound, but which was found to be entirely organic. It was removed

[1] Friedel and Crafts, *Ann. chim. phys.*, [6] 1, 516 (1884).
[2] *Ann. chim. phys.*, [6] 11, 268 (1887).
[3] *Ann.*, 235, 174 (1886).
[4] *J. Chem. Soc.*, 85, 213 (1904).

and recrystallised from a mixture of benzene and chloroform. The puri-
fied substance melted at 286°–287°. It was a light yellow crystalline
powder.

Found: C = 89.60 and H = 8.45. Calc. for tetramethylanthracene: C = 92.30
and H = 7.70.

It gave all the general characteristics of an anthracene derivative,
notwithstanding the fact that Dewar and Jones[1] were unable to prepare
anthracene derivatives from mesitylene by the Friedel-Crafts reaction. It
seems perfectly evident that hexamethylanthracene cannot be made directly
from mesitylene and any other reagent. On the contrary, a tetramethyl
compound is not impossible, as two of the methyl groups, one from each of
two mesitylene molecules, might be the means of connecting the two
molecules as an anthracene derivative. This seems to have happened,
forming a tetramethylanthracene which must necessarily be either a
$1:3:6:8$ or a $2.4:7:9$ derivative. It is interesting to note
that the melting point corresponds closely with the melting point of tetra-
methylanthracene as mentioned above m. p. above 280°.

The filtered ether extract was then distilled and the distillates collected
in two parts, the first between 90°–200° and the second between 200°–
350°. Above this practically nothing would distil over. At a very high
temperature it began to decompose. The first distillate consisted of
small amounts of benzene, toluene, xylene and mesitylene. The second
distillate at first appeared as an oily liquid from which crystals formed on
standing. These were separated out by adding ether, whereupon the
oily substance immediately dissolved, leaving the crystals behind. They
were removed, washed with ether and recrystallized from a mixture of
hot alcohol and ether. Thus obtained, the crystals appeared as white
monoclinic plates with a m. p. of 129°–130°.

Analysis and general characteristics showed that the substance was
dimesitylmethane prepared by Baeyer[2] from mesitylene, formaldehyde
and sulfuric acid.

The ether solution containing the oil was warmed in order to remove
the ether and then distilled. The first fraction, boiling between 170°–
325°, was so small that no attempt was made to examine it.

Durene.—The fraction between 325°–355° consisted of solids together
with some oil Both were very soluble in all the common solvents. They
were finally separated by placing on unglazed porcelain plates which readily
absorbed the oil leaving the crystals behind. The crystals were finally
purified by crystallizing from 95% alcohol. Thus purified they melted
at 79°–80°. This differed from any of the other compounds.

Found: C = 90.22 and H = 9.65. Calc. for $C_{10}H_{14}$ = 89.6 and H = 10.4.

[1] *J. Chem. Soc.*, **85**, 218 (1904).

[2] *Ber.*, **5**, 1098 (1872).

There seems to be no doubt but that this substance is durene, notwithstanding the results of the analysis. In order to further identify it the dibromo and dinitro compounds were made and found to agree in every respect with the dibromo and dinitro compounds prepared by Anschütz.

That the above reaction with mesitylene is complex is evident from the formation of benzene, toluene, xylene and durene. This unusual reaction was observed by Anschütz,[1] who first showed that benzene homologs are formed from a single benzene derivative by the action of aluminium chloride. But as already stated, no anthracene derivatives had ever been prepared from mesitylene. There can be no doubt but the compound described above is an anthracene derivative. We have represented it as a tetramethyl compound, although analysis really agrees better for a hexamethyl derivative. We have so represented it because a hexa compound can only be formed from a isomer of mesitylene like pseudo-cumene or hemellithene. While we have not succeeded in identifying these latter compounds, both are within the range of possibility, and a hexamethyl derivative could therefore be formed. Experiments along this line are now under way.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN

GAS ANALYSES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES.[2]

BY G. A. BURRELL AND F. M. SEIBERT.

This paper describes experiments that resulted in the separation of a natural gas sample into the individual paraffin hydrocarbons present. This had not been accomplished hitherto.

Natural gases may contain only methane as the combustible constituent or may be mixtures that contain large quantities of the higher gaseous paraffins. In some samples the latter predominate. In addition, there may be vapors of the liquid paraffin hydrocarbons present, sometimes enough to warrant the installation of a plant for their extraction. The natural gas used in Pittsburgh is a complex mixture, and is typical of gas that is supplied to many cities to the extent of billions of cubic feet per year. The exact composition of this gas is of importance to the Bureau of Mines because it is used in testing explosives, safety lamps, electrical mining machinery, and other mining appliances. By the scheme shown herein, it is also possible to determine more closely the quantity of the vapors of the liquid paraffins in a natural gas mixture than has been possible heretofore.

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[1] *Ann.*, 235, 178–190 (1886).

[2] Paper presented before the spring meeting of the American Chemical Society, April 7–10, 1914, by permission of the Director of the Bureau of Mines.

Gases that contain enough of these vapors are compressed and cooled at many plants and the condensate sold as gasoline.

It is generally known that ordinary combustion gas analyses give but little indication regarding the individual hydrocarbons present in a natural gas mixture. Only the two predominating paraffins are shown.

In the experiments reported herein, natural gas was first liquefied by means of liquid air and the different paraffin hydrocarbons separated by properly adjusting temperatures and removing the various fractions with a mercury pump. These fractions were analyzed by the ordinary slow combustion method. Advantage was taken of the work of P. Lebeau and A. Damiens,[1] who prepared various mixtures of the gaseous paraffins, liquefied them and partially separated them. This work is in advance over their work in that the separation was made into single constituents. The important part of this paper, however, is the application of the work to the determination of the constituents of natural gas. Such a separation is possible because, in the liquid condition, the boiling points of the gaseous paraffins are rather widely separated. These boiling points follow: Methane, $-160°$, ethane, $-93°$, propane, $-45°$; N butane, $+1°$; and isobutane $-10°$. The two butanes were not separated. In order to finish the work with fractions large enough for accurate analyses, the experiment given herein was started with about $1^1/_2$ liters of gas (1531 cc.). Other experiments were performed with various natural gases in which smaller quantities were used. The sample, as analyzed by the ordinary slow combustion method, contained the following constituents

Methane	79 2%
Ethane	19 6
Nitrogen	1 2
Total	100 0

There is also about 0.03 per cent. of carbon dioxide in the gas mixture. Carbon monoxide, hydrogen and olefine hydrocarbons are not present.

Experimental Procedure.—Fig. 1 shows the general arrangement of the apparatus. The Töpler pump is on the left of the photograph. (A) is a small glass vessel used for holding the liquefied gases. It could be enclosed in the Dewar flask (B). Surrounding this Dewar flask is shown another and larger one. This arrangement was adopted in order to provide better insulation than was afforded by only one flask, although the work can be conducted with only one Dewar flask. The gas sample, prior to liquefaction, was measured by weighing the water displaced from the glass vessel (C) then transferred to the gas buret (D) and from there passed into the liquefying bulb (A). At (E) is shown a mercury manometer for registering pressures in the pump. At the base of the

[1] *Compt. rend.*, **156**, 325 (1913).
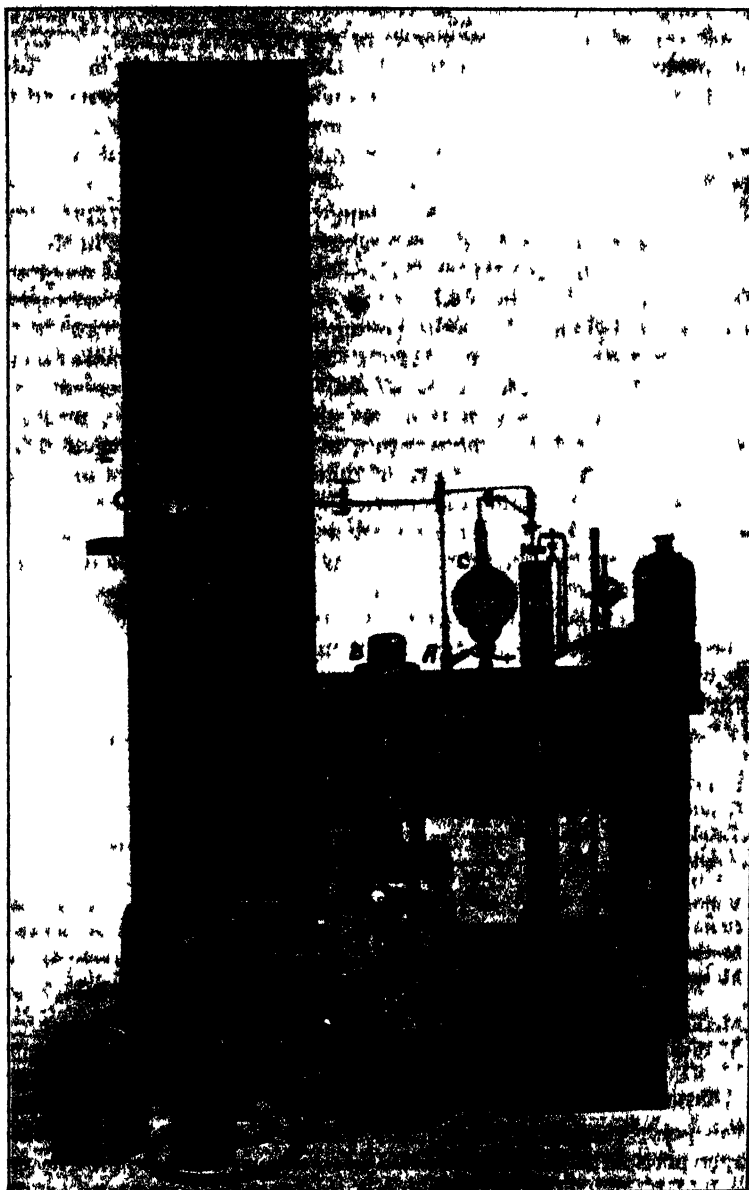
Fig 1 —Apparatus for the liquefaction and fractionation of gas mixtures

Töpler pump are shown the glass vessels for trapping the different gas fractions over mercury as they were removed.

The entire sample was first liquefied by means of liquid air. With the gas in the liquid condition, connection was made between it and the mercury pump and as much of the gas removed with the pump as possible. This process divided the original quantity into two portions; first, a gaseous portion, and second, a liquid residue.

In other words, the vapor pressure of liquid ethane (b. p.—93°) is so small at the temperature of liquid air that none could be detected in the distillate within the experimental error of making the analysis. It was found that, when liquid air was used which had stood for some time, so that its boiling point had risen near to the boiling point of oxygen (—183°), the methane and nitrogen were removed from the original mixture more quickly than when newly made liquid air was used. This is to be expected. The residue from this first fractionation was allowed to volatilize, measured and again liquefied at the temperature of liquid air. Connection was again made to the pump and more methane removed. In other words, although the residue from the first fraction was treated in exactly the same manner as the original sample more methane was obtained.

Upon volatilizing the entire residue, however, and again liquefying, a rearrangement of the solution occurred and chance for faster evaporation of this last methane portion was afforded. In no case could the last minute traces be obtained, so the attempts at complete recovery were stopped when it was found that only such a small proportion was being left behind as did not sensibly affect the results.

TABLE I.—ANALYSIS OF A PORTION OF THE TOTAL METHANE AND NITROGEN FRACTION.

	Cc.	Cc.
Sample taken	30.10	30.20
O_2 added	95.20	99.30
Total volume	125.30	129.50
Volume after combustion	66.30	70.10
Contraction due to combustion	59.00	59.40
Volume after CO_2 absorption	36.80	40.50
CO_2 produced by combustion	29.50	29.60
Methane from contraction[1]	29.44	29.64
Methane from CO_2[1]	29.59	29.67
	%.	%.
Methane from contraction	97.8	98.2
Methane from CO_2	98.3	98.2
Average per cent. methane	98.1	98.2

To this point, the first series of fractionations had reached a stage where the larger portion of the methane had been removed and where the first residue had been volatilized, reliquefied and pumped to obtain another

[1] Corrected for molecular volume of carbon dioxide.

small portion of methane. The residue from the second liquefaction was treated again in the same identical manner and more methane obtained. A further identical treatment resulted in no additional recovery of methane. No indication of methane was found in the ethane portion, within the error of making the analysis.

The distillate obtained by the above scheme undoubtedly contained a trace of ethane, but it was so small that it could not be detected by analysis. The analysis of a portion of the total methane and nitrogen fraction is given in Table I, above.

Second Series of Fractionations.

The next step in the process involved the separation of the ethane from the methane-free residue. This necessitated the employment of a temperature such that practically all of the ethane could be separated from the still higher paraffins, propane, the butanes, etc. The temperature used could not be too low, else the ethane itself could not be separated, nor so high as to also remove all the propane. A natural gas condensate, obtained from a natural gas gasoline plant by subjecting natural gas (casing head gas) from an oil well to a pressure of 250 lbs. per square inch and then cooling it to ordinary temperature, proved excellent, when cooled by liquid air, for obtaining low temperatures higher than the temperature of liquid air. This condensate is known in the natural gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes (especially the latter) as well as some of the ordinary gasoline constituents, the pentanes, hexanes, etc. Other substances tried for obtaining low temperatures, such as alcohol, ether, methyl, and ethyl chloride, etc., jellied so much at low temperatures that they could not be used satisfactorily. The mass did not remain of uniform temperature from top to bottom.

In order to obtain a temperature of $-145°$, for instance, the condensate was placed in a Dewar flask and stirred with a test tube into which liquid air was run until $-145°$ was reached. Upon removal of the liquid air the condensate warmed up very slowly, about $5°$ to $10°$ per hour, thereby affording sufficient time for the withdrawal of vapors from the liquefaction bulb. In separating ethane from the methane-free residue, the latter was first cooled to a temperature of $-145°$ and pumping was started and continued until the temperature had risen to $-125°$. By this process, there was obtained a distillate consisting of ethane and propane. In other words, some propane (b. p. $-45°$) is removed at $-125°$ as well as the ethane (b. p. $-93°$). The residue was then treated twice in the same manner, the final separation of the ethane being made at a temperature of $-155°$ to $-140°$. The temperature was purposely lowered to $-125°$ the first time to obtain practically all of the ethane as well as some propane, because it was found quicker to separate the

ethane from that part of the propane that came over than to attempt to pull off all of the ethane from the original residue.   All the ethane was obtained, there being only small quantities of propane remaining as a residue.   The analysis of a portion of the total ethane fraction is given in Table II.

TABLE II.—ANALYSIS OF A PORTION OF THE TOTAL ETHANE FRACTION

	(1) Cc	(2) Cc
Sample taken	25 50	20 30
O₂ added .	96 60	99 40
Total volume .	122 10	119 70
Volume after combustion	58 30	69 20
Contraction due to combustion	63 80	50 50
Volume after CO₂ absorption	7 20	28 70
CO₂ produced by combustion	51 10	40 50

According to the equation $C_2H_6 + 3.5\ O_2 = 2\ CO_2 + 3\ H_2O$, the contraction should be equal to the $CO_2 \times 1.25$.   In Analysis No 1 the contraction then becomes 51.1 cc. $\times$ 1.25 = 63.87 cc.   This corresponds well with the contraction actually observed, 63.80 cc.   In Analysis No. 2 the contraction   is   equal   to   40.50 cc. $\times$ 1.25 = 50.62.   The contraction actually observed is 50.50 cc.   In calculating the ethane from the carbon dioxide and contraction, use was made of equations that correct for the deviations of carbon dioxide and ethane from the ideal conditions,[1] as follows:

Analysis No 1
$$0\ 990\ C_2H_6 + 3\ 5\ O_2 = 1\ 992\ CO_2 + 3H_2O$$
cc. ethane = 0 396 $\times$ contraction = 25 26
cc ethane = 0 497 $\times$ CO₂ = 25 39

Analysis No. 2.
$$0\ 990\ C_2H_6 + 3\ 5\ O_2 = 1.994\ CO_2 + 3H_2O$$
cc ethane = 0 397 $\times$ contraction = 20 05
cc ethane = 0 496 $\times$ CO₂ = 20 09

Third Series of Fractionations.

The final residue from the second series of fractionations then contained propane and higher paraffins.

The ethane-free residue was next liquefied and pumped at a temperature that started at —125° and ended at —110°, the object being to remove practically all of the propane (b. p. —45°) and also some of the butanes (b. p. + 1° and —10°).   The residue from this operation was again treated in the same manner¹ to obtain any propane that still remained behind. It was thought that, if a temperature was used that would permit the distillation of an appreciable quantity of butane, practically all of the pro-

¹ Errors in gas analysis due to assuming that the molecular volumes of all gases are alike.   *Technical Paper* 54, U S. Bureau of Mines, by G. A. Burrell and F. M. Seibert.

pane should come over. The total distillate obtained in this manner was then liquefied and pumped at a temperature ranging from —135° to —120°. There resulted a distillate that consisted of propane only. In other words, propane can be separated from the butanes at a temperature below —135° and —120°

The analysis of a portion of the total propane fraction is given in Table III.

TABLE III —ANALYSIS OF A PORTION OF THE TOTAL PROPANE FRACTION

	Analysis No 1 Cc	Analysis No 2 Cc
Sample taken	12 60	13 30
O₂ added	93 80	97 20
Total volume	106 40	110 50
Volume after combustion	67 60	70 00
Contraction due to combustion	38 80	40 50
Volume after CO₂ absorption	28 50	29 70
Carbon dioxide produced	39 10	40 30

According to the equation $C_3H_8 + 5 O_2 = CO_2 + 4 H_2O$, the contraction — CO_2 = 0 0. In Analysis No. 1 38 8 cc — 39.1 cc. = —0.3 cc. and in Analysis No. 2 40 5 cc. — 40.3 cc. = 0.2 cc. The propane was calculated from the following corrected equation: $0.986 \ C_3H_8 + 5 O_2 = 2.991 \ CO_2 + 4 H_2O$

Then, according to Analysis No 1, the propane, when calculated from the contraction, is 0 329 × 38.80 = 12.76 cc. and, when calculated from the CO_2, is 0.329 × 39.10 = 12 86 cc.

According to Analysis No. 2 the propane, when calculated from the contraction, is 0 329 × 40.50 = 13.32 cc. and, when calculated from the CO_2, is 0 329 × 40.3 = 13.26 cc

In the case of both analyses the cc. of propane as calculated from the CO_2 and the contraction agree closely.

The value 0.986 or the molecular volume of propane at 0° and 760 mm. of mercury was calculated from van der Waals' equation

$$(P + a/V_2)(V - b) = RT$$

or

$$M/d_0 (1 + a)(1 - b) = R,$$

where M = molecular weight, d_0 = density at 0°.

Lebeau gives for a the value 0.01727 and for b 0.003770, from which

$$M/d_0 = 22.41/1.0133 = 22.116$$
$$22.116/22.412 = 0.986$$

This value, as far as the authors are aware, has never been determined experimentally as in the case of oxygen, methane, ethane, and carbon dioxide.

The same procedure was followed in the case of the propane separation as in the case of the ethane and methane separations. Distillates and residues were liquefied and pumped until no propane could be obtained.

The analysis of a portion of the final residue is given in Table IV. This should consist of butane only, providing no vapors of the liquid paraffins were present.

TABLE IV.—ANALYSIS OF A PORTION OF THE TOTAL BUTANE FRACTION.

	Cc
Sample taken . .	9 30
O₂ added	100 00
Total volume .	109 30
Volume after combustion	76 30
Contraction due to combustion	33 00
Volume after CO₂ absorption	39 30
CO₂ produced by combustion	37 00

From the equation $C_4H_{10} + 6.5\ O_2 = 4\ CO_2 + 5\ H_2O$, the contraction $\times 1.14 = CO_2$. From the above analysis, $33.0 \times 1.14 = 37.62$ cc. $37.62 - 37.00 = 0.62$ cc. difference.

The above analysis was calculated to butane only, and appears to be almost entirely this gas, but undoubtedly a very small proportion of the vapors of the liquid paraffins were contained in the mixture.

Vapor pressures obtained by means of a manometer attached to the pump furnished evidence which indicated when a separation had been accomplished. For instance, at the temperature of liquid air that had stood for some time (about −185°) the vapor pressure of the original hydrocarbon mixture was 63 mm. This vapor pressure was not the pressure of methane at that temperature; it remained near this value throughout the pumping until near the end, when it suddenly dropped to 0.0 mm. Then the pumping was stopped and the residue allowed to volatilize and again liquefied and pumping continued until no more distillate was obtained.

Three liquefactions of the residues were usually necessary for the removal of all the methane.

When the methane- and nitrogen-free residue was liquefied for the removal of the ethane, the vapor pressure of the mixture was about 2 mm. at −155° and about 4 mm. at −145°. When nearly all the ethane was removed and pressure dropped off suddenly to 0.0 mm., the pumping was stopped. The residue was again liquefied and treated in the same manner until all the ethane was removed. Three successive treatments of the residues were usually sufficient.

After the removal of the nitrogen, methane, and ethane from the mixture had been accomplished, it became necessary to separate the propane from the butanes, etc. This was accomplished at −130° to −120°. The vapor pressure at −130° was about 0.5 mm., and about 1 mm. at −125°. The pressure dropped suddenly to 0.0 mm. after nearly all the propane had been removed. The residues were then treated as previously described, until all the propane had been removed. The final residue con-

sisted of the butanes and any vapors of the liquid hydrocarbons that were present. There follows a list of the constituents found by the foregoing method.

Constituents	Cc		Per cent	
Nitrogen	23	8	1	6
Methane	1297	4	84	7
Ethane	144	5	9	4
Propane	46	1	3	0
Chiefly Butanes	19	2	1	3
Total	1531	0	100	0

In Table V is given a diagram of the various steps in the separation of a natural gas into its constituents by means of fractional distillation at low temperatures. It will be noted that the original volume of the sample was 1531.0 cc. The sample was first liquefied with liquid air and a distillate of 1311.3 cc. obtained with the mercury pump. A residue of 219.7 cc. was left behind. Both the residue and distillate were again treated at the temperature of liquid air. From the residue there was obtained 9.9 cc. more of methane, but no residue remained behind upon treating the distillate of 1311.3 cc. The sum total of 9.9 cc and 1311.3 cc. represented practically all of the methane and nitrogen in the natural gas sample. The distillate from the reliquefaction of the residue contained no methane, as determined by a further treatment at the temperature of liquid air.

After the methane had been separated, there remained a residue of 209.8 cc., consisting of ethane and higher paraffin hydrocarbons. This residue was cooled at temperatures ranging from —140° to —125° and as much gas removed with the pump as possible. Ethane and some propane were obtained (133.3 cc.) and a residue of 76.5 cc. remained behind. The distillate was then cooled to temperatures ranging from —150° to —135° and a distillate of 124.7 cc. obtained, and a residue of 8.6 cc. This 8.6 cc. residue was added to the 76.5 cc. residue and the total, 85.1 cc., cooled from —138° to —130° and pumped. The distillate of 34.8 cc. obtained was added to the 124 7 cc. distillate previously obtained and the total 159.5 cc. were cooled and pumped at a temperature that did not rise above —135°. There was obtained a distillate of 147.0 cc. and a residue of 12.5 cc. The 147.0 cc. distillate was then cooled and pumped at a temperature not higher than —140°. The distillate, 144.5 cc., was found to be pure ethane. The residue from this last treatment, 2.5 cc., was added to the rest of the methane- and ethane-free gas for the propane treatment. The separation of the propane and butane was carried on in a manner similar to the methane and ethane separations except for the use of lower temperatures.

Temperature measurements were made with two pentane thermometers. They agreed closely with each other and gave for the melting

TABLE V.—DIAGRAM SHOWING THE VARIOUS STEPS IN THE SEPARATION OF THE CONSTITUENTS IN NATURAL GAS BY MEANS OF FRACTIONAL DISTILLATION AT LOW TEMPERATURES.

ORIGINAL VOLUME.
1531.0 cc., liquefied at —185°, pressure 63 mm.

DISTILLATE
1311.3 cc., liquefied at —185°.

   distillate 1311.3 cc.

   residue 0.0 cc.

total methane and nitrogen, 1321 2 cc.

RESIDUE
219.7 cc., liquefied at —185°, pressure 2 mm.

   distillate 9.9 cc.

   residue 209 8 cc., liquefied at —185°, pressure 2 mm.

      distillate 0.0 cc.

      residue 209.8 cc., liquefied at —140° to —125°, at —140° pressure = 3 mm.

         distillate 133.3 cc., liquefied at —150° to —135°, at —150° pressure = 3 mm.

            distillate 124.7 cc.

            residue 8 6 cc.

         residue 76.5 cc.

159.5 cc.

liquefied at —155° to —135°,
at —155° pressure = 4 mm.

distillate
147.0 cc.

residue
12.5 cc.

liquefied at —155° to —140°,
at —140° pressure = 4 mm.

distillate
144.5 cc.

residue
2.5 cc.

total ethane

liquefied at —138° to —130°,
at —138° pressure = 6 mm.

distillate
34.8 cc.

residue
50.3 cc.,

liquefied at —130° to —120°,
at —130° pressure = 0 1 mm.

distillate
21.2 cc.

liquefied at —130° to —115°,
pressure at —115° = 1 mm.
pressure at —130° = 0.5 mm.

residue
29.1 cc., liquefied at —130° to —110°.

distillate
20.2 cc.

residue
1.0 cc.

liquefied at —135° to —120°,
at —135° pressure is below 0.1 mm.

distillate
10.9 cc.

residue
4.3 cc.

total propane
46.1 cc.

distillate
14.2 cc.

residue
14.9 cc.

total butane
19.2 cc.

point of chloroform —62°, of carbon disulfide —111°, and boiling point
of fresh liquid air —193°. The true melting point of chloroform is
—63.7°, and of carbon disulfide —111.6°.   All temperatures are in
degrees centigrade.

Summary.

A method of·separation of a natural gas into its paraffin hydrocarbons
is shown.   At a temperature of —185° to —190° the methane can
be removed.   The separation of the methane from the propane, butane,
etc., is conducted at temperatures ranging from —150° to —140°.
The propane is separated from the butanes, etc., at temperatures ranging
from —135° to —120°.

This method of separating a gaseous mixture into its constituents while
somewhat involved is the only known method in the case of some hydro-
carbons.   It can be extended to the separation of other gaseous mixtures.
The authors have separated other natural gases but the example given
herein is sufficient to describe the method.

DETERMINATION OF ARSENIC IN ORGANIC MATTER.
BY MARIAM VINOGRAD.

Oxidation of the Tissue for the Determination of Arsenic.—The use of
minimum quantities of reagents in oxidizing tissues for the Marsh test
is important, because it is very difficult to get certain reagents, such as
nitric acid, absolutely free from arsenic.   Another important consideration
is the prevention of the escape of the arsenic at the moment of carboni-
zation of the tissue, since, as is well known, arsenic is volatile at the tem-
perature of the oxidation.   Both of these difficulties were avoided by Ber-
trand[1], who showed that dried substance could be conveniently burned
in a Bertholet bomb with pure oxygen under 25 to 30 atmospheres pres-
sure.   The only disadvantage of Bertrand's method for general use is
that analytical laboratories are not ordinarily equipped with the Berthelot
apparatus.

Because of this fact, apparently, investigators have continued experi-
menting with methods of oxidation which could be carried out with the
facilities usually available.

Chittenden and Donaldson, in 1880, published a paper describing in
detail a simple method for partial oxidation of tissue with relatively small
amounts of nitric and sulfuric acids, the carbonaceous residue being ex-
tracted with water and used for the Marsh test.[2]   This method added

[1] Bertrand, *Ann. de l'Inst. Pasteur*, 1903, 581.
[2] *Am. Chem. J.*, 2, 255.

greatly to the reliability of the arsenic determinations in tissue. It required 100 grams of material, however, and the incomplete oxidation rendered the subsequent extraction of the charred residue rather laborious. Consequently other methods for the oxidation have continued to appear, not all of which can be regarded as improvements.

Karl Ulmann,[1] following Gautier's method, used a mixture of nitric and sulfuric acids in quantities twenty-fold the amount of tissue used. The tissue examined is heated for 6 to 36 hrs., according to its character, on a sand bath. A somewhat different method was used by Lockemann.[2] The tissue was first disintegrated by heating with an equal weight of a nitric-sulfuric acid mixture. Oxidation was completed by fusion with a mixture of sodium and potassium nitrates. These methods involve both the use of relatively large amount of reagents and the danger of volatilization of arsenic during the oxidation.

The application of the ordinary Carius' technique for organic analyses obviates both difficulties and we have found that it gives excellent results. With a sealed tube, loss by volatilization is impossible, and the application of high temperature and pressure enables one to complete the oxidation with a small amount of nitric acid. Thus, 1 cc. of nitric acid is sufficient to oxidize 3 cc. of blood serum, or 100 cc. of spinal fluid, or 0.5 g. of dry tissue. The method described in this communication has been used chiefly in the determination of arsenic in blood, tissues, and spinal fluid, after intravenous injections of salvarsan. The exact technique employed in testing these various substances is as follows:

The Oxidation of the Blood.—In the experiment under consideration 1 cc. of blood is put into a small test tube (about 6 cm. long and 5 mm. wide.) This tube is carefully lowered into a regular bomb tube, which contains 1 cc. of fuming nitric acid. The bomb tube is then sealed in the ordinary way and heated slowly to 260°. At this temperature the heating is continued for an hour or two, at the end of which time the oxidation is complete. The tube then contains a clear liquid of yellowish color, due to the nitrous oxides. Any arsenic present will have been completely converted into arsenic acid. The combustion oven with the tube is cooled to room temperature, and the pressure is released in the usual manner by melting the capillary point. The tube is then opened and the contents washed with distilled water into a 200 cc. Jena Kjeldahl flask. The liquid is evaporated until only about 15 cc. are left. This is then further heated with 4 to 5 cc. of sulfuric acid until all traces of nitric acid are driven out, as nitric acid appears to be a disturbing agent in the process

[1] Karl Ulmann, "Zur Frage der Parasitotropie und Toxizitat des Salvarsans," *Wien. klin. Wochschr.*, 1913, No 6.

[2] Lockemann, "Uber den Arsennachweis mit dem Marschschen Apparat," *Z. angew. Chem.*, 18, 416 (1905).

of the determination of arsenic. In order to dilute this sulfuric acid, it is washed with a known quantity of distilled water (about 10 cc.) into a small graduated cylinder. Distilled water is then added to make up the total volume to seven times the volume of the original sulfuric acid.

Oxidation of the Tissues.—The different parts, such as lungs, liver, kidneys and parts of the muscles, are dried thoroughly in porcelain dishes on a water bath, and are then ground to a powder. Up to 0.5 g. of dry tissue is taken for oxidation by the method described above. In case the tissue sample is small enough to go into the test tube, drying is unnecessary.

The Oxidation of Spinal Fluid.—In the determination of arsenic in the spinal fluid, 100 cc. of the fluid are put into a small, round-bottom crystallizing dish and evaporated nearly to dryness on a water bath. The semi-solid residue is transferred, as completely as possible, to a small tube (about 6 cm. long and $1/2$ cm. wide). The remaining traces are washed with 1 cc. of fuming nitric acid into the bomb tube. The small tube is lowered into the bomb tube, which is then sealed. The rest of the process is identical with the treatment of the blood, described above.

Determination of Arsenic in the Solution by Sanger and Black's Method.— The application of Gutzeit's color reaction, of hydrogen arsenite with mercuric chloride paper, to the determination of small amounts of arsenic has been carefully worked out by Sanger and Black.[1] We will describe briefly the use of the method with solutions of oxidized tissues prepared as above described.

The apparatus is shown in Fig. 1. A bottle with a wide opening, of 40 cc. capacity, is stoppered with an arsenic-free, two-hole rubber stopper (prepared by boiling for an hour in 5% NaOH solution). A 5 mm. glass funnel-tube, drawn out to 1 mm. at the lower end, passes through one perforation of the stopper and reaches to the bottom of the bottle. Through the other perforation passes a bent piece of glass tubing, through which the gases can escape. This tube is connected by means of a small calcium chloride tube, in which lies, next to the stopper, a rolled strip of filter paper saturated with lead acetate to absorb hydrogen sulfide. The bulb of the tube is filled with absorbing cotton, dried in a desiccator. The long part of the tube, the diameter of which is 5 mm., carries a strip of drawing paper, about 5 mm. wide and 7 cm. long, saturated with a 5% solution of mercuric chloride. These strips are prepared by immersing them in the mercury solution and then drying at room temperature. They are kept in a test tube containing, on the bottom, several pieces of calcium chloride, covered with absorbing cotton. In order to make the generation of hydrogen continuous, a sheet of platinum is placed on the bottom of the apparatus. On top of the platinum are placed 3 g. of zinc,

[1] Sanger and Black, *Proc. Am. Acad.*, **43**, 297 (1907); *J. Soc. Chem. Ind.*, **26**, 1115 (1907); *Z. anorg. Chem.*, **58**, 121 (1908).

then, 10 cc. of special diluted 'sulfuric acid (see above) are poured in.   Ten minutes after this, the solution to be tested for arsenic is poured in.   The presence of arsenic is determined by the coloring of the end of the strip nearest the bulb. The quantity of arsenic is determined by the depth to which the yellowish orange color attains. The method is sensitive to less than 0.001 mg. of arsenic.

All the glass and porcelain apparatus used must be tested for arsenic, and only such taken as proves to be free from it. The sulfuric acid is usually found to be free from arsenic. The greatest difficulty was encountered with the zinc, but the brand called "Bertha Spelter," from the New Jersey Zinc Com-

Fig. 1.

pany of New York, recommended by Sanger and Black, proved to be arsenic-free.   The zinc was delivered to us in large pieces. These were melted in French clay crucibles and the molten mass poured into water, where it solidified in small pieces suitable for the experiments.

NEW YORK, N. Y.
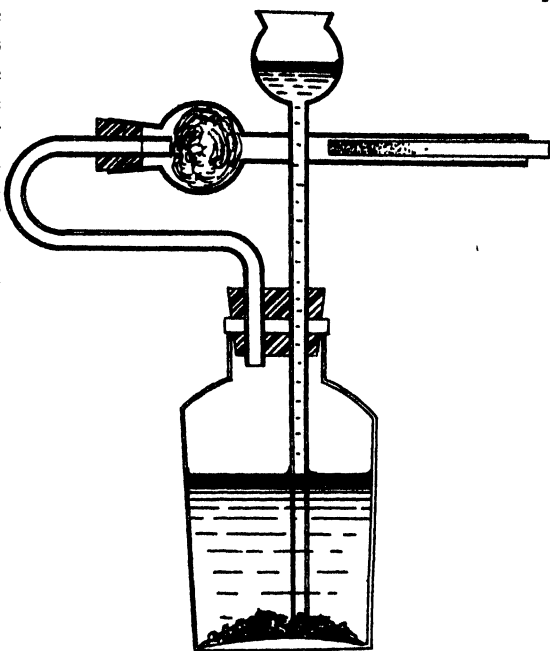
PARTITION OF THE NITROGEN OF PLANT, YEAST, AND MEAT EXTRACTS.

BY F. C. COOK [1]
Received April 22, 1914.

Introduction.

An investigation of the nitrogenous and other constituents of meat extracts, bouillon cubes, and plant extracts was recently reported by Micko.[2] In previous papers he[3] discussed the purine bases of meat and

[1] Physiological Chemist, Animal Physiological Chemistry Laboratory.

[2] Z. Nahr. Genussm., 26, 321 (1913).

[3] Ibid , 5, 193 (1902); 6, 781 (1903).

yeast extracts and stated that xanthine and hypoxanthine predominate in meat extracts, while adenine and guanine predominate in yeast extracts. The writer[1] has published analyses and tests for distinguishing yeast extracts from meat extracts and has recommended the creatinine test as the most satisfactory. In a recent article he[2] stated that meat extracts give higher total nitrogen results than plant extracts and suggested the value of the creatinine and phosphoric acid figures in determining the relative amount of meat extract present in bouillon cubes.

This study was undertaken in order to find some means of identifying the three classes of extracts, by determining the nitrogen constituents present, and to obtain information in regard to the nitrogenous composition of these extracts.

Experimental.

Description of Extracts.—Five samples of meat extract, one of yeast extract, and seven of plant extract, all of them commercial samples of unknown history, were examined. All had a pasty consistency and similar odor and taste. The meat extracts were semi-solid extracts, which are usually prepared by evaporating in vacuum pans the liquor obtained in the packing houses during the cooking of beef preparatory to canning. The yeast extract was prepared from exhausted beer yeast. The yeast, after being washed, yielded on hydrolysis a liquor which was subjected to the same general treatment as the liquor from the beef. The plant or vegetable extracts are more completely hydrolyzed products than either meat or yeast extracts. Such extracts are prepared from soy beans and concentrated extracts of vegetables and herbs, as leek, celery, parsnip and onion with the addition of sodium chloride after concentration in vacuum.

Description of Methods.—The total nitrogen[3] was determined by the Kjeldahl-Gunning method.[4] The samples were digested for four hours, as better results for total nitrogen are obtained when the digestion is carried on for four hours than for shorter periods.

Ammonia was determined by the Folin and Macallum[5] method as outlined for urine. The precipitation with acid-alcohol has not been compared directly with other precipitation methods. This method has been used by Rippetoe to distinguish plant from meat extracts and was suggested by him to the writer. He outlines the procedure as follows:

"Transfer 10 cc. of an aqueous solution of the extract (10 cc. equal 1 g.) to a 200 cc. glass stoppered measuring cylinder, add 1.2 cc. of a 12% hydrochloric acid solution, mix and add absolute alcohol to 200 cc. mark, mix thoroughly and set aside for several

[1] U. S. Dept. Agr. Bureau of Chemistry, *Bull.* 114 and *Cir.* 62.

[2] *J. Ind. Eng. Chem.*, 5, No. 12 (1913).

[3] The nitrogen determinations were made by the Nitrogen Laboratory of this Bureau.

[4] U. S. Dept. Agr. Bureau of Chemistry, *Bull.* 107, Rev.

[5] *J. Biol. Chem.*, 11, 523 (1912).

At 20° to 25°. If necessary, make up to mark, filter, and transfer 100 cc. to a Kjeldahl flask, evaporate alcohol on water bath and determine nitrogen in residue "

The tannin salt precipitation[1] was carried out, using tannic acid of the highest purity obtainable, as required by this method. The writer in applying this reagent has always used a pure tannic acid which is stated to have been prepared from Chinese gall nuts.

Solutions of all the extracts were treated according to the formol titration method of Sörensen[2] and the Van Slyke[3] method for amino nitrogen. The dark color of the extracts interfered with the end points of the Sörensen method, and the results obtained were not satisfactory. The ammonia was determined in a separate sample and the results in the table are corrected for ammonia. The Van Slyke method was successfully applied to water solutions of the extracts.

TABULATION OF RESULTS —PARTITION OF THE NITROGEN OF PLANT, YEAST AND MEAT EXTRACTS

Variety and sample number	Total nitrogen Per cent	Ammonia nitrogen	Total creatin-ine nitrogen			Nitrogen in phosphotungstic acid filtrate	Nitrogen in acid-alcohol filtrate	Nitrogen in tannin-salt filtrate	Amino nitrogen Van S
Meat extracts									
1	9 56	2 62	22 49	3 35	7 64	78 04	54 91	10 94	18 50
2	9 65	2 49	22 59	3 52	6 84	78 45	55 85	10 94	18 23
3	7 68	1 56	32 42	2 86	71 35	100 00	73 04	10 63	15 63
4	9 65		29 01	4 92	49 74	76 73	59 37	10 27[4]	15 54
5	7 49		27 50	0 13		89 19	64 21	9 53	17 89
Yeast extract									
6	5 35	2 43	0	11 22	49 96	72 15	56 07	17 64	32 71
Plant extracts									
7	5 23	7 46	0	0 42	85 85	100 00	94 46	36 71	65 77
8	6 34	12 78	0	0 44	84 08	99 69	89 95	36 43	57 41
9	6 33		0	0 25		100 00	83 41	30 64	45 18
10	6 27	11 32	0	0 44	83 25	98 56	92 66	35 88	67 78 ·
11	6 47	6 03	0		63 68	100 00	84 54	30 75	44 20
12	6 08	12 98	0	0 46	84 04	99 67	92 76	35 85	61 18
13	6 63	10 56	0	0 23	86 88	99 25	91 40	34 08	57 31

Total creatinine was determined by the Benedict-Myers[6] autoclave

[1] J Am Chem Soc, 12, 1485 (1906)
[2] Biochem Zeit, 7, 45 (1908)
[3] J Biol Chem, 9, 185 (1911)
[4] 15% of ammonia nitrogen included
[5] No correction for ammonia, no determination
[6] Am J Physiol, 18, 397 (1907)

method, and purine nitrogen according to Schittenhelm,[1] as applied to meat extracts by the writer.[2]

Discussion of Results.

As seen in the table, the meat extracts gave higher total nitrogen results than the plant or yeast extracts. Nevertheless, more ammonia was obtained from the plant than from the meat extracts. Micko reports 4.22% of total nitrogen, as ammonia nitrogen, in a sample of meat extract and states that the ammonia nitrogen should never exceed 6% of the total nitrogen of a meat extract. His results were obtained by distilling with magnesium oxide and are considerably higher than the ammonia results given in the table, which were obtained by the Folin method. The magnesium oxide method is recognized as yielding more than the ammonia nitrogen.[3] The results for the plant extracts vary from 6.03 to 12.98% of the total nitrogen and are so much higher than the meat extract figures that the ammonia determination becomes of value in distinguishing a plant from a meat extract.

The plant and yeast extracts gave no biuret reaction, and are therefore more completely hydrolyzed products than the meat extracts, which gave this test. Meat extract Samples 3 and 5 were exhausted before this test was made.

Only the total creatinine present in the meat extracts was determined. Some creatine, as well as creatinine, is present, but, both having a common origin, namely, the creatine of the muscle, there is no object in determining the relative amounts of these two substances. No creatine or creatinine was found in the plant and yeast extracts. Their absence makes this determination of the greatest value in distinguishing a yeast or plant extract from a meat extract. The total creatinine nitrogen comprises from 22.49% to 32.42% of the total nitrogen of the meat extracts reported in the table. Micko, in referring to the creatinine content of meat extracts, stated that 20%, or more, of the nitrogen of a meat extract is present as creatinine nitrogen.

The purine nitrogen results for the plant extracts were exceedingly low, the highest yielding but 0.46% of the total nitrogen as purine nitrogen. The yeast extract contained 11.22% of its nitrogen as purine nitrogen, and the meat extracts, with the exception of extract No. 5, gave from 2.86 to 4.92% of their nitrogen in this form. Micko reports 7.3% of the nitrogen of a meat extract as purine nitrogen and states that the purine nitrogen of meat extracts should comprise from 6 to 8% of the total nitrogen. These figures are higher than the results reported on the table, which were obtained by the Schittenhelm method. The method employed by Micko

[1] *Z. Physiol Chem.*, **39**, 199 (1903).
[2] U. S. Dept. Agr , Bur of Chem., *Bull.* **114.**
[3] *Ibid.*, **132**, p. 20

was the method of the "Codex Alimentarius Austriacus." The results for purine nitrogen are interesting, not only in showing analytical differences in the plant and meat extracts, but also for the reason that no determinations for purine nitrogen in plant extracts have been reported in the literature[1] so far as the writer knows.

Comparison of the Precipitation Methods.—The plant extracts gave a much larger percentage of nitrogen in the phosphotungstic acid filtrate than the yeast or meat extracts. All of the nitrogen of the plant extracts was present in the hydrochloric acid-alcohol filtrate. This was true of meat extract No. 3 in the table. Similarly the tannin-salt reagent, when applied to plant extracts, showed most of the nitrogen in the filtrate. The yeast extract gave a cloudy filtrate from the acid-alcohol and tannin-salt precipitations; all the other extracts gave clear filtrates in these cases.

Comparison of Formol and Van Slyke Methods.—The formol method gave lower figures for amino nitrogen than the gasometric method of Van Slyke. As the formol method should include both the amino nitrogen and ammonia nitrogen, we would expect to obtain higher results than with the Van Slyke method, which includes the simple aliphatic amino nitrogen and 15% of the ammonia nitrogen. The formol method is based on the idea that for each carboxyl group there is a corresponding amino group. The amino groups combine with the formaldehyde and the carboxyl groups are free to be titrated with standard alkali. That this does not hold true in these extracts is apparent from the results obtained. The results by the formol and Van Slyke methods, however, show the same general tendencies as the precipitation methods, that is, where the precipitating reagents gave a low percentage of nitrogen in the filtrate (amino nitrogen) low amino nitrogen figures were obtained by these two methods. From the point of view of accuracy the Van Slyke method is undoubtedly superior to the formol method, which apparently gives results which are far too low when applied to extracts, as has been done here; and that, in spite of the tendency to overrun the end point on account of the dark colored solution of the extracts.

Summary.

There is great variation in the precipitating power of the different reagents compared. Photosphungstic acid precipitated the highest, tannin-salt the next highest, and acid-alcohol the lowest percentage of the nitrogen of the extracts examined.

The formol titration method of Sörensen gave lower results for the amino nitrogen in meat, plant, and yeast extracts than the Van Slyke method.

All of these methods showed that a larger percentage of the nitrogen

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[1] Since the above was written Micko's paper (*Löc. cit.*) appeared, which contains four purine nitrogen results for plant extracts.

was present in a more completely hydrolyzed state, in the plant than in the yeast or meat extracts.

No creatine or creatinine and very little purine nitrogen was found in the plant extracts. The yeast extract showed high purine nitrogen and no creatine or creatinine. Plant and yeast extracts gave no biuret reaction but the meat extracts examined gave this reaction.

All of the nitrogen of the plant extracts was found in the filtrate after applying acid-alcohol, and consists chiefly of mono-amino acids and ammonia. About 25% of the nitrogen of the meat and yeast extracts is precipitated by acid-alcohol. The plant extracts yield a much larger percentage of nitrogen as ammonia nitrogen than the meat or yeast extracts.

In differentiating these three classes of extracts, the creatinine, ammonia, purine nitrogen and acid-alcohol determinations are of value to the food analyst.

BUREAU OF CHEMISTRY,
DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

STUDIES ON THE CHEMISTRY OF EMBRYONIC GROWTH. II. COMPARATIVE ANALYSES OF THE EGGS AND OF THE NEWLY-HATCHED LARVAE OF THE GIANT SALAMANDER, CRYPTOBRANCHUS ALLEGHENIENSIS.

BY ROSS AIKEN GORTNER.

Introduction.

The Problem.—The purpose of this investigation is identical with that of the first paper in this series (Gortner, 1913), *i. e.*, to determine whether the "chemical compounds which are present in the egg enter the growing tissues in the same form in which they are laid down in the egg, or whether synthetic changes are also taking place so that the material which is present in the egg is used, not in its original form but in a modified condition."

The distribution of the nitrogenous compounds in the various stages of development offers the easiest method of attack. In the preceding paper I presented a study of the nitrogen distribution in fresh eggs of the brook trout (*Satelinus fontinalis* L.), and in embryos and young fry at different stages in their development. The present paper is devoted to a somewhat similar study of the eggs and of the newly-hatched larvae of the salamander, *Cryptobranchus Allegheniensis*, Daudin.

The Material.—The eggs of *Cryptobranchus* have proved to be a excellent material for chemical studies. In most amphibian eggs the tough

jell which surrounds the egg makes the preparation of the first sample very difficult, which fact, combined with the usual small size of amphibian eggs, probably accounts for our lack of knowledge of the chemistry of these eggs. Until very recently only a few eggs of *Cryptobranchus* had ever been found but I was fortunate enough to be assisted in my search for the eggs by Dr. Bertram G. Smith, the only person who has ever found them in abundance, and I wish to take this opportunity of thanking him for his many courtesies.

The eggs were secured in the northwestern part of Pennsylvania in the early part of September. Each female deposits about 450 eggs in a hole underneath a rock. The eggs average about 6.2 mm. in diameter are bright yellow in color, a rather deep yellow at the lower pole grading to a pale yellow at the upper pole, and are inclosed in a gelatinous outer envelope about 18 mm. in diameter. These envelopes are joined in a long chain by a thin connecting cord so that the eggs as found resemble a long string of beads. By cutting the envelope with scissors the eggs are easily removed. The vitelline membrane surrounding the yolk mass is very delicate, so that the eggs after removal from the outer envelope must be handled in water with a large mouth pipette to avoid breaking them. For this reason I was unable to secure data as to the weight of the egg before drying. After drying the eggs average about 0.058 g.

The eggs which were secured in advanced stage of development were allowed to remain in shallow dishes just covered with filtered lake water until a part had hatched. Smith (1912) gives the time necessary for development to hatching as about six weeks. Those which had not hatched (but which would have hatched within 48 hours) were released from the envelope by cutting with scissors. The newly-hatched larvae are about 23–25 mm. in length and have a dry weight of approximately 0.057 gram.

Experimental.

The Method.—Sample 1 consisted of 150 eggs in early cleavage stages; sample 2 of 100 larvae at hatching. The eggs and larvae were placed in weighing bottles and dried in a water oven at the temperature of boiling water. Undoubtedly there are objections to this method of drying, but I believe that this is preferable to drying *in vacuo* at a low temperature, since, in the latter, a certain amount of autolysis is almost sure to take place. Autolysis is prevented by both the high temperature and by the rapid drying of a water oven and I do not believe that the nitrogen ratios are altered by such treatment.

After ascertaining the dry weight, the eggs and larvae were removed as completely as possible[1] to an extraction thimble and extracted with anhydrous ether in a Soxhlet apparatus for 48 hours. The ether from the

[1] A very small amount, 0.33% of the total in the case of the eggs and 0.15% in the case of the larvae, persisted in sticking to the walls and sides of the weighing bottles.

eggs became deep golden yellow in color while that from the larvae was colored a yellowish red. Six hours after the extraction began the liquid syphoning was colorless. The ether was evaporated on a water bath and the residue dried to constant weight at 90°. The residue from the eggs was more fluid than that from the larvæ and the color differences were the same as those of the ethereal solution.

The residues remaining in the extraction thimbles were next extracted with absolute alcohol in a Soxhlet apparatus for 48 hrs. After the ether extraction had been completed the residue in the extraction thimble was still bright yellow and this *second yellow pigment* proved readily soluble in alcohol, being all removed at the end of 6 hrs.' extraction, leaving the residue a dull gray. The alcohol was evaporated on a water bath and the residue dried at 90°. This fraction is designated as "ether insoluble but alcohol soluble."

The residue remaining from the alcohol extraction was dried at 90° and weighed, this being the "protein portion" of the eggs and larvæ.

The nitrogen partition was determined on the ether soluble and on the ether-insoluble-but-alcohol-soluble portions as follows·

To the residues in the flasks I added 50 cc. HCl of 1.115 sp. g. and boiled the mixture on an electric hot plate for 18 hrs.[1] The HCl was removed, as completely as possible, by distillation on a water bath under a pressure of 20 mm. and 150 cc. of water and 100 cc. of 95% alcohol added to the residue in the flask. An excess of a 10% suspension of $Ca(OH)_2$ was then added and the ammonia nitrogen distilled off into standard acid under a vacuum of 20 mm. at 40–45°.

The mixture remaining in the flask, after the removal of the ammonia nitrogen, was filtered and the residue washed with hot water until chlorides were removed. The nitrogen in the residue on the filter was determined by the Kjeldahl method and recorded as humin nitrogen. In this fraction is included not only the true "humin" nitrogen, but also the nitrogen of any nitrogenous lipin which has not been rendered water soluble by the acid hydrolysis, as well as any basic nitrogenous compound which forms an insoluble calcium salt.

The filtrate from the humin nitrogen was evaporated to a small volume

[1] Of course there are objections to this hydrolysis with acids, but, since the nitrogenous compounds are of the nature of lipins, if they were not hydrolyzed with acid (or alkali) the greater part, if not all, of the nitrogen would be found water insoluble and therefore appearing in the humin nitrogen fraction as a result of adsorption and precipitation with the Ca(OH)₂ By acid hydrolysis under constant conditions one should obtain *comparative* results, and after study of the behavior of the known nitrogenous lipins and other nitrogenous compounds which would be dissolved by either the ether or the alcohol extraction to acid hydrolysis (which study I hope to make soon) it may be possible to determine, to some extent, the nature of the compounds with which we are dealing.

under diminished pressure and then washed into a 200 cc. Erlenmeyer flask. Nine cc. of conc. HCl and sufficient water were added to make the volume 100 cc. and, after heating, 7.5 g. of phosphotungstic acid were added and the mixture set aside in a cool place for 48 hours to permit the basic phosphotungstates to separate. The precipitate was washed as directed by Van Slyke (1911) and the nitrogen content of the bases determined by Kjeldahl.

The entire filtrate from the bases was concentrated in a Kjeldahl flask and the non-basic nitrogen determined by Kjeldahl's method after the addition of 35 cc. conc. H_2SO_4, 15 g. K_2SO_4, and 0.25 g. $CuSO_4$.

The "protein fraction" of the eggs and larvae was analyzed in exact conformance with my modification (as regards dilutions, etc.) of Van Slykes' method (1911, 1912) as already described in THIS JOURNAL (Gortner, 1913), so that a second detailed description is unnecessary.

The analytical data follow:

Sample 1.—150 eggs removed from the uterus and fertilized artificially at 4:30 p.m. Sept. 6th. These eggs were allowed to develop until 3 p.m. Sept. 9th, when they were carefully removed from their envelopes and the drying was begun.

Weight of 150 eggs dry at 100° = 8.7381 g.

Ether soluble portion = 1.6772 g.
Nitrogen in ether-soluble portion = 0.00378 g. divided as follows:
    Ammonia N = 0 30 cc 0 1 *N* acid indicating 0 00028 g. N in 100 eggs.
    Humin N = 1.20 cc. 0.1 *N* acid indicating 0.00112 g. N in 100 eggs.
    Basic N = 0.30 cc. 0.1 *N* acid indicating 0.00028 g. N in 100 eggs.
    Non-basic N = 0.90 cc. 0.1 *N* acid indicating 0.00084 g. N in 100 eggs.

Alcohol-soluble-but-ether-insoluble-portion = 0.9945 g.
Nitrogen in alcohol fraction = 0.0105 g., divided as follows:
    Ammonia N = 0.15 cc. 0.1 *N* acid indicating 0.00014 g. N in 100 eggs.
    Humin N = 1.80 cc. 0.1 *N* acid indicating 0.00168 g N in 100 eggs.
    Basic N = 4.10 cc. 0.1 *N* acid indicating 0.00382 g. N in 100 eggs.
    Non-basic N = 1.45 cc. 0.1 *N* acid indicating 0.00136 g. N in 100 eggs.

Protein fraction (insoluble in ether or alcohol) = 6.0385 g.[2]
    Nitrogen in the protein fraction = 0.8631 g., distributed as follows:
    Ammonia N = 62.4 cc. 0.1 *N* acid indicating 0.0582 g. N in 100 eggs.
    Humin N = 14.1 cc. 0.1 *N* acid indicating 0.0132 g. N in 100 eggs.

[1] It was impossible to begin the drying at an earlier stage because of the necessity of transporting the material from western Pennsylvania to the laboratory. There should be some delay before eggs are taken for development studies in order to see whether the eggs are fertile and would develop. The eggs forming my sample were probably in Stage 8 (Smith 1912) and had developed to probably 256 cells, perhaps slightly more. It is highly improbable that this amount of development could have caused any chemical changes large enough to be detected by my methods of analysis.

[2] A slight loss occurred in removing the dried eggs from the weighing bottle to the extraction thimble so that the ether + alcohol + protein fractions only total 99.67% of the dry weight.

The filtrate from the humin was made to 200 cc. and nitrogen in the filtrate from the humin determined on 10 cc. portions, (1) 26.90 and (2) 27.10 cc. 0.1 N acid indicating 0.5040 g. N in the filtrate from the humin in 100 eggs.

The bases were precipitated by the addition of 18 cc. conc. HCl and 15 g. of phosphotungstic acid to 160 cc. of the above solution.

Arginine N (on $\frac{1}{2}$ of the bases) = 17.0 cc. 0.1 N acid indicating 0.0793 g. N in 100 eggs.

Total basic N (on $\frac{1}{2}$ bases + arginine) = 74.15 cc. 0.1 N acid indicating 0.1730 g. N in 100 eggs.

Amino N in bases (from 5 cc.) = 19.25 cc. N at 23° and 768 mm. (from 7.5 cc.) = 29.2 cc. N at 22° and 768 mm. indicating 0.0916 g. amino N in the bases of 100 eggs.

Cystine N (on 10 cc.) = 0.0050 g BaSO₄ indicating 0.00126 g N in 100 eggs.

Histidine N (calc.) = 0.0329 g. in 100 eggs.

Lysine N (calc.) = 0.0595 g. in 100 eggs.

Nitrogen in the filtrate from the bases (made to 200 cc.) = (on 25 cc. portions) 35.20 and 35.60 cc. 0.1 N acid indicating 0.3304 g, N in 100 eggs.

Amino N in the filtrate from the bases = (on 10 cc.) 33.9 cc. N at 21.5° and 749 mm. and 33.8 cc. N at 21.5° and 750 mm. indicating 0.3142 g. amino N in 100 eggs.

These data calculated to *per cent. of the total nitrogen of the egg* form the fourth column, and the *weight of nitrogen in g.* forms the first column in Table II.

Sample II.—100 larvae at hatching. Some had just hatched while others were released from the membrane.

Weight of 100 larvae dry at 100° = 5.7285 g.

Ether soluble portion = 1.2747 g.

Nitrogen in ether soluble portion = 0.00455 g. divided as follows:

Ammonia N = 0.45 cc. 0.1 N acid indicating 0.00063 g. N.

Humin N = 1.60 cc. 0.1 N acid indicating 0.00224 g. N.

Basic N = 0.20 cc. 0.1 N acid indicating 0.00028 g. N.

Non-basic N = 1.0 cc. 0.1 N acid indicating 0.0014 g. N.

Alcohol-soluble-but-ether-insoluble portion = 0.6179 g.

Nitrogen in alcohol soluble portion = 0.0111 g. distributed as follows.

Ammonia N = 0.10 cc. N acid indicating 0.00014 g. N.

Humin N = 1.70 cc. 0.1 N acid indicating 0.00238 g. N

Basic N = 3.50 cc. 0.1 N acid indicating 0.0049 g. N.

Non-basic N = 2.65 cc. 0.1 N acid indicating 0.0037 g. N.

Protein residue (insoluble in alcohol and ether) = 3.8278 g.[1]

Nitrogen in the protein residue = 0.5688 g., distributed as follows·

Ammonia N = 42.60 cc. 0.1 N acid indicating 0.0596 g. N.

Humin N = 9.70 cc. 0.1 N acid indicating 0.0136 g. N.

The filtrate from the humin was made to 200 cc. and the nitrogen content determined on 10 cc. portions = 17.7 and 17.7 cc. 0.1 N acid, indicating 0.4956 g. N in the filtrate from the humin.

[1] The ether + alcohol + protein fractions total only 99.85% of the dry weight because of a slight loss which occurred by incomplete removal from the weighing bottle.

The bases were precipitated from 160 cc. of the above solution, and were finally made to 50 cc. volume.

Arginine N (on $1/2$ bases) = 11.6 cc. 0.1 N acid indicating 0.0812 g. N.

Total N in the bases (on $1/2$ bases + arginine N) = 49.05 cc. 0.1 N acid indicating 0.1717 g. N.

Amino N in bases = (on 5 cc.) 13.10 cc. N at 23° and 768 mm. and (on 8.5 cc.) 21.5 cc. N at 24° and 769 mm. indicating 0.0911 g. N.

Cystine N = 0.0044 g. BaSO₄ (on 10 cc.) indicating 0.00165 g. N.

Histidine N (calc.) = 0.0288 g. N.

Lysine N (calc.) = 0.0600 g. N

The filtrate from the bases was made to 200 cc. and nitrogen found on 25 cc. portions = 22.80 and 22.80 cc. 0.1 N acid indicating 0.3192 g. N.

Amino N in the filtrate from the bases = (on 10 cc.) 21.3 cc. N at 21° and 764 mm. and 21.3 cc. N at 20.5° and 763 mm. indicating 0.3035 g. N.

These data calculated to *per cent. of the total nitrogen* in the larvae form the fifth column and the *percentage change from egg to larvae* forms the sixth column in Table II. *The weight of the nitrogen in grams* per 100 larvae forms the second column and the *change of nitrogen* in grams in the development of the egg to the hatching stage forms the third column in Table II.

TABLE I.—COMPARATIVE ANALYSES OF CRYPTOBRANCHUS EGGS AND OF THE LARVAE AT HATCHING.

	Weight in grams.			Percentages.		
	100 eggs.	100 larvae.	Change.	Eggs.	Larvae.	Change.
Dry weight	5.8254	5.7285	—0 0969	...	...	—1.66%
Ether sol.	1 1182	1.2747	+0 1565	19.19	22.25	+3.06
Ether insol. but alcohol sol.	0.6630	0.6179	—0.0451	11.38	10.78	—0.60
Protein	4.0256	3.8278	—0 1978	69.10	66.82	—2 28
N content	0.5849	0.5845	—0.0004	. .	. .	. .
N in ether	0.00252	0.00455	+0.00203	0 44	0.78	+0.34
N in alcohol.	0.0070	0.0111	+0.0041	1.20	1 90	+0.70
N in protein	0 5754	0.5688	—0 0066	98 37	97.30	—1.04
% N in protein fraction..	...	...	. .	14.30	14 86	+0.56

Discussion.

Although the analyses recorded in the preceding tables agree in most entries so well that we could conclude that the samples analyzed were duplicates, there are a few entries which show changes which are certainly significant. A careful study of these data has convinced me that all, or nearly all, of the nitrogen ratios are altered to some extent as embryonic growth progresses, but that the monoamino acids are the more generally utilized. Such a conclusion is in excellent agreement with my earlier findings (Gortner, 1913).

During the development there was a loss of 1.66% of the dry weight (0.0969 g. per 100 larvae) which must be attributed to carbon dioxide and water, inasmuch as no nitrogen was lost during this period of growth.

TABLE II.—DISTRIBUTION OF NITROGEN IN 100 CRYPTOBRANCHUS EGGS AND LARVAE.

		In grains			In percentage		
		Eggs.	Larvae.	Change.	Eggs.	Larvae.	Change.
Ether soluble	Ammonia N	0.00028	0.00063	+0.00035	0.048	0.108	+0.06
	Humin N	0.00112	0.00224	+0.00112	0.191	0.383	+0.192
	Basic N	0.00028	0.00028	...	0.048	0.048	...
	Non-basic N	0.00084	0.00140	+0.00056	0.114	0.239	+0.125
Ether insoluble, alcohol soluble	Ammonia N	0.00014	0.00014	...	0.024	0.024	...
	Humin N	0.00168	0.00238	+0.00070	0.287	0.407	+0.120
	Basic N	0.00382	0.00490	+0.00108	0.654	0.838	+0.184
	Non-basic N	0.00136	0.00371	+0.00235	0.231	0.635	+0.404
Protein fraction	Ammonia N	0.03824	0.05964	+0.0014	9.956	10.21	+0.254
	Humin N	0.01316	0.01358	+0 0042	2.25	2.324	+0.074
	Basic N	0.1729	0.1717	−0.0013			...
	Non-basic N	0.3304	0.3192	−0.0112			...
	Arginine N	0.07932	0.08121	+0.0019	13.56	13.90	+0.34
	Cystine N	0.00196	0.00165	+0.0004	0.213	0.282	+0.07
	Lysine N	0.05946	0.0600	+0.00054	10.16	10.27	+0.11
	Histidine N	0.03292	0.0288	−0.0041	5.63	4.93	−0.70
	Amino N filt. from bases	0.3142	0.3035	−0.0107	53.73	51.92	−1.81
	Non-NH₃ N in filt.	0.0162	0.0157	−0.0005	2.76	2.686	−0.074
Total N in samples		0.58492	0.58450	−0.00042			...
N recovered in analyses		0.5843	0.57976		99.856	99.204	
Loss of N in analyses		0.00062	0.00474	...			...

Accompanying this loss in weight there is a very marked *gain of fats* equal to 3.06% of the egg weight and to an increase of 14% of the fat already present in the egg.

Tangl and Farkas (1904) have observed a similar synthesis of fat in developing trout embryos and explain this finding by the assumption that there are present, in the egg, glycoproteins which are broken down to carbon dioxide, water, glycogen, fat, and "all of the nitrogen of the protein is retained in the organism in the form of urea (or uric acid)," the difference in energy content being the "Entwicklungsarbeit." I believe that their hypothesis is in part correct, *i. e.*, that the energy of development comes from a carbohydrate nucleus, but other parts of their suggestion I find to be erroneous.

Tangl and Farkas submit no proof for their contention that the nitrogen of the protein is converted into urea (or uric acid). In discussing this phase of their work in my earlier paper, I showed that, in all probability, no considerable quantity of either urea or uric acid was present in the young trout at hatching and that, therefore, their hypothesis did not hold in its entirety. In this series of analyses of *Cryptobranchus* eggs and larvae there can be no doubt that no urea is formed and in all probability none, or at most only a trace, of the nitrogen is converted into uric acid.

The behavior of urea and of uric acid to extraction with ether and alcohol was first investigated. The statement that urea is insoluble in ether and that uric acid is insoluble in both ether and alcohol seems to find no exception in the solubility literature. As I have shown elsewhere, (Gortner 1914), *this statement is not true*, for although urea is practically insoluble (approx. 0.0004 g. in 100 cc.) in anhydrous ether nevertheless *as much as 0.0720 g. is dissolved in the course of a 48-hour extraction*, and while uric acid is still more insoluble in absolute alcohol (approx. 0.00008 g. in 100 cc.), *as much as 0.0260 g. is extracted in 48 hours* in a Soxhlet apparatus.

We should look, therefore, for an increase in *Ammonia N* in the ether soluble fraction if urea has been formed within the organism, and the observed increase, while possibly significant, is only 0.3% of the required amount.[1] The entire gain of ammonia N in all three fractions analyzed would be only 1.6% of the expected urea N.

Uric acid would be extracted, at least in part, by the absolute alcohol and an increase in ammonia N should follow a synthesis of uric acid, since I have shown that 15% of the uric acid nitrogen is split off as ammonia

[1] Tangl and Farkas found a gain of 0.38 g. of fat and an energy loss of 3.46 kg. Cal. in the course of the development of 518 trout eggs and theorize that 1.67 g. of glycoprotein (9.7 Cal.) must be broken down to 0.38 g. fat (3.5 Cal.), 0.30 g. glycogen (1.3 Cal.) and 0.57 g. urea (1.40 Cal.) the difference in calculated heat values being 3.5 Cal. Using their figures I should find 0.234 g. of urea containing 0.109 g. N due to a synthesis of 0.1565 g. fat.

by acid hydrolysis (Gortner 1913, p. 642). There is no gain in ammonia N in the alcohol extract and the total gain of N in this fraction is only an insignificant part of the theoretical uric acid nitrogen. *We must there- fore conclude that no appreciable amount of urea or of uric acid is formed in Cryptobranchus during embryonic growth.*

The analyses show, further, that the origin of the fats synthesized is, in a large measure at least, to be found in the protein fraction but that *it is not a simple protein which has been altered*, for, although there is a loss of 0.1978 g. from the protein fraction, the nitrogen content of the lost portion is only 3.33%, leaving a remaining protein residue with a relatively increased nitrogen content.

The above facts would seem to support only one argument, *i. e.*, that there is present in the eggs of *Cryptobranchus* a carbohydrate nucleus either free (glycogen) or more probably in the form of a glycoprotein (ovomucoid?). During the process of development this carbohydrate is broken down to carbon dioxide and water with the consequent releasing of energy for the "Entwicklungsarbeit," but the breaking down of the carbohydrate proceeds more rapidly than is necessary to provide the energy of development and, as a result, the surplus energy is stored in the form of fat. If the carbohydrate is a part of a protein molecule, the amino acids are not "burned" but are utilized in part in their original form and in part to furnish the nitrogen for lecithin and other nitrogenous compounds necessary for the development of the growing embryo.

Several additional points demand brief comments. There is a gain of nitrogen in both the ether soluble and the ether-insoluble-but-alcohol-soluble fractions. It seems possible that the gain in the ether soluble fraction is due to a synthesis of lecithins such as Tichmiroff (1885) observed in developing eggs of the silk worm (*Bombyx mori*). It is very evident from the nitrogen partition that the nitrogen in the alcohol extract is all, or nearly all, from basic nitrogenous compounds, probably pyrimidine or purine bases. Kossel (1886) and Mendel and Leavenworth (1908) have shown that purine bases are synthesized as embryonic growth progresses in hen and duck eggs. Unfortunately we know too little of the solubilities of the purine and pyrimidine bases *under conditions of continuous extraction* to decide which compounds would be found in the ether extract, the alcohol extract, or which should be insoluble in both alcohol and ether. •

One surprising result (to me) of these analyses was the large percentage of "ether insoluble but alcohol soluble" compounds in the egg. I know of no data dealing with this fraction (as regards non-nitrogenous compounds) and should consider it a great favor if any reader could call to my attention such data as may exist or suggest the possible nature of these substances,

Summary.

1. The eggs of *Cryptobranchus* contain two yellow pigments, one being soluble in ether and the other insoluble in ether but soluble in absolute alcohol.

2. There is a total loss of dry weight (CO_2 and H_2O) during the development of 100 eggs to the hatching stage of 0.0969 g. or 1.66% of the dry weight.

3. There is a *gain* of fats during development of 0.1565 g. per 100 eggs this being equal to an increase of 14% of the fat already present in the egg.

4. There is a loss of 0.0451 g. from the fraction insoluble in ether but soluble in absolute alcohol. The significance of this loss is unknown.

5. There is a loss of 0.1978 g. from the protein fraction, but in all probability this is not a loss of a simple protein but of a carbohydrate radical which has been broken down to form fat, etc.

6. There is neither loss or gain of total nitrogen during development.

7. There is a gain of nitrogen in the ether soluble portion of 0.00203 g. This would indicate a synthesis of 0.1174 g. of di-steryl-lecithin (1.73% N), providing all of the nitrogen in the ether soluble portion is counted as lecithin.

8. There is a gain of 0.0041 g. of nitrogen in the ether-insoluble-but-alcohol-soluble fraction. The nitrogen in this fraction is largely basic nitrogen, probably purine or pyrimidine bases.

9. There is a loss of 0.0066 g. nitrogen from the protein fraction. Nearly all of this loss comes from the mon-amino acids.

10. There is considerable evidence that the nitrogen ratios in the protein fraction are not fixed quantities but that some amino acids are more necessary for the development of the embryo than are others and as a result there is a continuous breaking down and recombining of the resulting radicals into new compounds. For example, the gain observed for Arginine N, although small, is probably significant.

11. No appreciable amount of either urea or of uric acid is formed during embryonic development of *Cryptobranchus*.

12. It seems probable that there is, in the eggs of *Cryptobranchus*, a carbohydrate nucleus either free (glycogen) or combined in the form of a glycoprotein and that during the process of embryonic growth this carbohydrate is broken down to carbon dioxide and water with a consequent liberation of energy for the "Entwicklungsarbeit," but the breaking down of the carbohydrate proceeds more rapidly than the needs of growth demand, with the result that the surplus energy is stored as fat.

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COLD SPRING HARBOR,
LONG ISLAND, N. Y.

THE INVERSION OF SUCROSE BY INVERTASE. VIII. AN IMPROVED METHOD FOR PREPARING STRONG INVERTASE SOLUTIONS FROM TOP OR BOTTOM YEAST.

BY C. S. HUDSON.[1]

The Clerget method for estimating sucrose depends upon the measurement of the change in optical rotation which accompanies the hydrolysi of the sugar. Hydrochloric acid is generally used as the hydrolyst although it is known to hydrolyze inulin, raffinose, and some other carbohydrates under the mildest conditions that will accomplish the inversion of sucrose.

In 1881, it was proposed by Kjeldahl[2] to use the enzyme invertase in place of hydrochloric acid in the Clerget method because invertase was regarded as a more nearly specific hydrolyst for sucrose. Although it is now understood that invertase hydrolyzes raffinose, gentianose, and stachyose as well, it seems that these sugars are derivatives of sucrose and that invertase may still be strictly regarded as a specific hydrolyst of sucrose and certain of its immediate derivatives. Kjeldahl used, in one procedure, an aqueous extract of yeast to hydrolyze sucrose, and, in an alternative one, a portion of yeast added to the sucrose solution which was kept at 52° with a little thymol added to prevent alcoholic fermentation. As invertase is rapidly, though incompletely, extracted from yeast by water, its action can be obtained by either of these procedures. Kjeldahl's untimely death prevented the further development of this excellent analytical

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[1] Contribution from the Division of Carbohydrate Investigations, Bureau of Chemistry.

[2] Compt. rend. Carlsberg Laboratoire, *Copenhagen*, 1, 14–49 (1881).

method and it came into notice next in 1886, when O'Sullivan and Tompson,[1] without knowing of Kjeldahl's procedure, recommended one which is substantially the same, the only difference being that thymol is not used and the mixture of yeast and sucrose solution is kept at 55°, at which high temperature alcoholic fermentation is prevented and the action of invertase aided.

Ling and Baker,[2] and more recently Ogilvie,[3] have followed with success O'Sullivan and Tompson's procedure in the estimation of sucrose in a variety of cane and beet products. In 1910, the author[4] sought to improve the method by using in place of yeast, a purified aqueous extract of yeast which had strong inverting power. The idea was that the main objection to the use of invertase, as a hydrolyst in analytical work, came from the uncertainty attaching to the use of a substance of such varying properties as yeast. It seemed that the method would become more dependable if a procedure could be found for preparing a stock solution of invertase which would keep well, have a definitely known, and high, inverting power, and be as free as possible from impurities.[5]

The first method which was tried was the extraction of invertase from living yeast by water, as had been done by Kjeldahl, but the inverting powers of the extracts were too low. The slow autolysis of yeast during several weeks keeping at 10° to 20°, which had been recommended by O'Sullivan and Tompson as a method for preparing aqueous solutions of invertase, was next tried, but while these experiments were in progress, H. E. Berger and the author observed that the liquefaction of pressed yeast, which is one of the changes that is noticeable during its slow autolysis, can be brought about in a few minutes by allowing the vapors of ether or chloroform to act upon living yeast, and a test showed that the fluid which could be filtered from the liquefied yeast had strong inverting power.[6] It became possible, therefore, to substitute in place of O'Sullivan and Tompson's method of preparing invertase by very slow autolysis an excellent and rapid procedure in which the autolysis is accomplished in a few hours by the action of chloroform upon fresh yeast. It was found that

[1] *J. Chem. Soc.*, **49,** 64 (1886); **59,** 46 (1891).

[2] *J. Soc. Chem. Ind.* **17,** 111-4 (1898).

[3] *Ibid*, **30,** 62-4 (1911); *Int. Sugar J.,* **14,** 89-93 (1912).

[4] *J. Ind. Eng. Chem.,* **2,** 143-C (1910).

[5] One recalls, in this connection, O'Sullivan and Tompson's statement, made in 1891 (*Loc. cit.*), that "The estimation of cane sugar by means of invertase is, without doubt, a perfectly satisfactory process. The only disadvantage consists in the difficulty of preparing the invertase. Until the recent publication of our paper on invertase, this objection was practically fatal, and it still forms a great drawback to the universal application of the process, as it takes at least three weeks to prepare invertase by our method."

[6] Salkowski (*Z. physiol. Chem.*, **13,** 520 (1889)) has shown that sucrose is rapidly inverted by yeast in the presence of chloroform water.

the aqueous solution which could be filtered from the liquefied yeast could be purified with only a small loss in its inverting power, by clarifying it with an excess of neutral lead acetate, filtering off the precipitate, and removing the excess of lead from the filtrate with potassium oxalate or hydrogen sulfide. This purification of the invertase solution by the use of neutral lead acetate has been confirmed by Euler.[1] The purified solution was then dialyzed thoroughly and used as a stock reagent for inverting sucrose.

As ether and chloroform had each caused yeast to autolyze very rapidly and give up its invertase, it became of interest to test the action of other neutral volatile liquids for the purpose of learning which substance would cause yeast to liberate the most invertase. Ether, chloroform, ethyl acetate, acetone, carbon tetrachloride, carbon disulfide, kerosene oil, and toluene were tried, and it was found that the rapidity of the liquefaction of the yeast varied considerably and that toluene caused the liberation of far more invertase than did chloroform and that toluene was not surpassed by any other of the liquids in this respect.[2] Accordingly, I have substituted toluene for chloroform in the method for preparing invertase, with an important increase in the inverting strength of the resulting purified extracts. These extracts we now use as stock reagents for the hydrolysis of sucrose.

The procedure which is used for the preparation of invertase solutions may be understood from the following record. Ten kilos of pressed top fermentation yeast, from the Corby Company, Langdon, D. C., were kneaded well with 10 liters of tap water and 500 cc. of toluene[3] at room temperature. Liquefaction of the yeast was noticeable in a few hours

[1] *Z. physiol. Chem.*, **73**, 338 (1911); also "General Chemistry of the Enzymes," English, 1912 edition, p. 26.

[2] After our experiments had been completed, it was learned that such volatile liquids have been used in "processes for obtaining the contents of yeast cells," according to the British patent to Ransford, No. 8722, April 27, 1901, and the United States patents to Hess, No. 785,733 and No. 785,734, March 28, 1905. The processes which are described in these patents are evidently intended for extracting soluble albumin from yeast and attention was not directed to obtaining a maximum yield of enzymes such as invertase. In these patents, there is no distinction made between the low extraction of invertase which results from the action of chloroform and the high extraction which results from the action of toluene. We have found that the use of ethyl acetate, which is mentioned in Hess's patent as particularly suitable for obtaining the contents of yeast cells, gives an extract which is very weak in invertase and quite insuitable for our purpose.

[3] Nelson and Born (THIS JOURNAL, **36**, 395 (1914)) have recently prepared invertase from yeast by allowing the compressed yeast to autolyze slowly at room temperature during two to six weeks, toluene being added to prevent bacterial growth. This procedure differs from the one here described in that we thoroughly saturate the yeast with toluene, after mixing it with an equal weight of water to aid the saturation, and thereby obtain a far more rapid autolysis than they produced.

and on the third day a test of the activity of the filtered extract from the autolysis showed that 5 cc. of it would invert half the sucrose in 50 cc. of a 9% sucrose solution, acidified with 2 drops of glacial acetic acid and kept at 30°, in 5.9 minutes. Other experiments have repeatedly shown that the extract exhibits considerable activity on the day immediately following that upon which the autolysis was started, but we were unable to test this extract so early. The yeast was allowed to autolyze two days longer, when it was found that the extract would invert half the sucrose, under the conditions recorded above, in 5.6 minutes. On the third day the value was found to be 6.4 minutes, showing some loss in activity. Neutral lead acetate was then added until no further precipitate formed and the activity was thereby reduced to 6.8 minutes. Upon treating the filtrate with hydrogen sulfide to remove the excess of lead, the activity rose to 6.3 minutes, which shows that there is no considerable permanent loss in activity due to the use of lead acetate as a clarification agent and that the temporary loss of activity from the first precipitation is caused by a retarding action of the excess of dissolved lead acetate on the invertase. It was found, in confirmation of this view, that the addition of lead acetate to a purified invertase solution, in which no precipitate formed, caused a marked loss in activity.

The preparation of invertase from bottom fermentation or brewer's yeast by the method which has been described shows some points of difference, which may be understood from the following record. Twelve kilos of pressed brewer's yeast from the Heurich Brewing Company, Washington, D. C., were kneaded well with 12 liters of tap water and 750 cc. of toluene at room temperature. On the succeeding day the filtered extract showed an activity of 7.2 minutes and on successive following days the number of minutes required for half inversion were 5.7, 4.3, 3.8 and 3.4. At this point, the lead acetate was added and the activity became 4.0, at which value it remained after the excess of lead had been precipitated by hydrogen sulfide. It will be observed that brewer's yeast furnishes an invertase solution which is almost twice as strong as that yielded by top yeast.

The next step in the preparation of the solutions of invertase is a thorough dialysis. It is advisable to carry this out immediately because the extracts are markedly acid before dialysis and often lose activity rapidly in this condition. Neutralization causes a formation of color which does not disappear in a subsequent dialysis. The most suitable membrane for the dialysis which has been found is a collodion sac which may be formed on the inside of a glass cylinder about 5 cm. in diameter and 35 cm. long, resembling a large test tube. The collodion solution, which is of Pharmacopeia strength, is poured into the dry test tube, filling it, and wetting

the walls evenly. The solution is then poured back into the stock bottle, and the film which coats the test tube is allowed to dry with even thickness while the tube is gently turned during five or ten minutes. When the film has dried until it is no longer sticky, the test tube is filled with water and the film soaked for a few minutes. The water is then poured out, the film is loosened at the top from the tube, and water is run in between film and tube at the loosened place. The pressure of the water loosens the entire film and it may readily be removed from the test tube. In order to dialyze the invertase solutions, they are poured into the collodion sacs and these are immersed in running tap water, a layer of toluene to retard bacterial action being on the surface of the solutions. Dialysis is frequently complete overnight, the time required depending much upon the quality of the membrane.

The dialyzed solutions are colorless, without taste or odor, develop none upon boiling, and yield on the average about two-tenths of 1% of solid material when evaporated to dryness on a water bath. Numerous tests have shown that there is no loss of invertase during the dialysis, but the absorption of water by the solutions causes some dilution. The dialyzed solutions may be preserved with toluene at room temperature and in distinction from the dialyzed solutions of other enzymes, they preserve their activity well. During the first month's keeping the solutions show no loss in activity and at the end of a year the activity is about half lost. Their inverting strength is enough to cause the hydrolysis of sucrose solutions over night, under usual analytical conditions, and is many fold larger than that of the invertase solution which was previously recommended, made by hastening the autolysis of yeast with chloroform. The dialyzed solutions we have concentrated and even dried without loss in activity by boiling at not over $30°$ in a vacuum. This work will be described later, when it is hoped that a description of the solid material, which must include the invertase, can be made.

It may be noted that, though the dialyzed invertase solutions have an unusually strong power of hydrolyzing sucrose, test has shown them to be without any action on α-methyl-glucoside, thus confirming the generally accepted view that this substance is not hydrolyzed by invertase. They show no action upon solutions of maltose or lactose. An interesting observation concerning raffinose was noted. H. S. Paine and T. S. Harding noticed that an invertase solution, which the latter prepared from *top* fermentation yeast, obtained from the yeast factory of the Corby Company, Langdon, D. C., changed the specific rotation of a solution of anhydrous raffinose from $+123°$ to $+63.9°$. On the other hand, a similar invertase solution which was prepared from *bottom* fermentation yeast, obtained from the Heurich Brewing Company, Washington, D. C., changed

the rotation from $+123°$ to $+14.9°$.[1] This interesting difference we attribute to the presence of an enzyme in the invertase solution from bottom yeast which carried the hydrolysis of raffinose a step beyond that which invertase causes. Probably invertase and melibiase are in the solution which was prepared from bottom yeast, while melibiase is lacking in that made from top yeast. This view corresponds to the well known fact that top yeast ferments raffinose to alcohol and melibiose, and bottom yeast ferments it completely to alcohol. T. S. Harding and the writer have worked out an analytical method for estimating raffinose in solutions containing other sugars, by utilizing the difference in rotation which is observed when the solution is acted upon, first by invertase from top yeast, and then by invertase and melibiase from bottom yeast.

Bureau of Chemistry, Department of Agriculture,
Washington, D C

THE INVERSION OF SUCROSE BY INVERTASE. IX. IS THE REACTION REVERSIBLE?[2]

By C S. Hudson and H S Paine.[3]
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The synthetic production of sucrose by various plants, ultimately from carbon dioxide and water, is a firmly founded fact, though it is not positively known what substances are the intermediate products in the synthesis. Many plants also synthesize an enzyme of unknown composition called invertase, which can accomplish the hydrolysis of sucrose to glucose and fructose. Thus the synthesis of sucrose may proceed in plants along with its decomposition by invertase. If the last stage in the synthesis should prove to be the uniting of glucose and fructose to yield sucrose, this change would represent the reverse reaction to the hydrolysis of sucrose by invertase. It has been suggested at various times that the enzyme invertase can accomplish such a synthesis of sucrose from glucose and fructose, and that therefore the inversion of sucrose by invertase is a balanced or reversible reaction. The present investigation was undertaken for the purpose of obtaining experimental evidence upon this question, partly because the subject is of some general interest and partly

[1] The values $63.9°$ and $14.9°$ correspond almost exactly to those ($64 1°$ and $14.9°$) which have been calculated by C. A. Browne ("Handbook of Sugar Analysis," p. 737) for the two steps that are to be expected in the hydrolysis of raffinose, which may be represented as the reactions

$$C_{18}H_{32}O_{16} + 2H_2O = C_{12}H_{22}O_{11} + C_6H_{12}O_6 + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{12}O_6.$$
(raffinose)   (melibiose) (fructose)   (glucose) (galactose) (fructose)
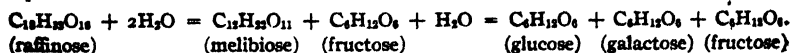
[2] Read at the Minneapolis meeting of the American Chemical Society in December, 1910.

[3] Contribution from the Division of Carbohydrate Investigations, Bureau of Chemistry.

because it became necessary to know whether invertase accomplishes a complete hydrolysis of sucrose in connection with an investigation on the possible use of this enzyme in the quantitative estimation of sucrose.[1]

Repetition of Osaka's Experiments.—In a recent article, Osaka[2] claims to have shown by accurate experiments that the well known hydrolysis of sucrose by acids, which has heretofore been regarded as an irreversible reaction, is really reversible, and indeed to the extent of an easily detectable amount, 1%, under certain favorable conditions. If this conclusion of Osaka is correct, it gives much ground, from a theoretical standpoint, for the view that the inversion of sucrose by invertase is also a reversible reaction, because both acid and enzyme are to be regarded as catalysts of the hydrolysis, and, since the equilibria of the better investigated reversible reactions are not changed by catalysts,[3] though the rate of reaction is, it might be expected that invertase will cause the synthesis of sucrose from glucose and fructose if the other catalysts, acids, do so. It is necessary to consider the details of the procedure in Osaka's experiments, although they are rather complicated. Osaka reasoned that, since the synthesis of sucrose from invert sugar is a combination of two substances (glucose and fructose) to produce one, it should proceed more favorably in concentrated than in dilute solutions. All of Osaka's experiments are similar and we have therefore selected for careful repetition the one in which he obtained the best indication of reversibility during acid hydrolysis. This experiment concerns the hydrolysis of sucrose by hydrochloric acid in an aqueous solution of about 61% sugar strength, which is the highest concentration that Osaka studied. He describes this experiment as follows:

"Twenty grams of cane sugar were introduced into a weighed measuring flask of 25 cc. capacity and dissolved in a small quantity of water by warming. When cold, 5 cc. of 2.5 N hydrochloric acid were added and the solution diluted to almost 25 cc. A small piece of camphor was then added to the solution[4] and the flask left in a thermostat at 25° over night. On the next day water, at 25°, was added to make exactly 25 cc. and the flask and contents were weighed. About 5 cc. of the solution were taken out from each of the duplicate solutions into two weighed measuring flasks of 25 cc. capacity and weighed. About 4 cc. of 2.5 N hydrochloric acid were added to each of them, and the solutions diluted to about 25 cc. The four diluted solutions thus prepared, together with the two original solutions, were again left in the thermostat over night.

[1] *J. Ind. Eng. Chem.*, 2, 143–6 (1910).

[2] *J. Col. Sci., Imp Univ Tokyo*, 25, Art 1 (1908)

[3] van't Hoff, "Die Chemische Dynamik," p. 210 (1898)

[4] This addition was presumably for the purpose of preventing the growth of microörganisms though the high acidity of the solution accomplishes this effectively, according to our experience. *H and P.*

"On the next day about 5 cc. of the two original solutions were taken out, each into two weighed measuring flasks of 25 cc. capacity, and weighed. In order to prevent its further inversion on dilution, 3.4 g. of sodium acetate were added to the solutions taken out, which were then diluted to the mark. The same amount of the salt was also introduced into each of the solutions diluted the day previous, to make them as nearly as possible similar to those newly prepared[1] and then the solutions were further diluted to the mark. It was ascertained by experiment that a small difference in the concentrations of hydrochloric acid exerts no perceptible influence on the optical rotations of the sugar solutions. The eight dilute solutions thus prepared were then subjected to polarimetric observations a polarization apparatus after Landolt being used with a Lippich polarizer. In order to obtain the mean value of the rotations of the solutions of the same treatment and to be able to compare those of solutions of different treatments with each other, it was assumed that, within narrow limits of concentration, as in the case in hand, the rotations are proportional to the concentrations of the solutions. The average amount of the solutions taken out in eight instances was 6.3776 g. The rotation of this weight of solution diluted to 25 cc. was calculated from the weights and respective rotations (when diluted to 25 cc. final volume) of the eight samples above to be viz:

Inverted in orig soln	Inverted in dil soln
—6 325	—6 587
—6 307	—6 625
—6 310	—6 586
—6 311	—6 578
Mean,[2] —6 313	Mean, —6 594

"Twenty-five cc. of the original solution weighed 32.793 g. and contained 20 g. sugar, so that 6.3776 g. of the solution contained 3.8896 g. The same amount of sugar was dissolved in water with the addition of sodium acetate and hydrochloric acid so as to make the solution similar to those in the other cases, diluted to 25 cc. and polarized. The mean of the two polarizations was +20.099. Thus the degree of the inversion in the original solution in percentage is as follows:

$$\frac{20.099 + 6.313}{20.099 + 6.594} \times 100 = 98.9\%.\text{''}$$

[1] One observes that though the two sets of solutions were thus made similar in respect to salt content, they differed in that the set which represented inversion in concentrated solution had stood one day longer in a highly acid condition. This matter is discussed later, on page 1575, et seq H and P

[2] These readings presumably refer to a tube length of 20 cm and to circular degrees and sodium light H. and P

From these data Osaka concluded that 1.1% of sucrose was synthesized during the experiment.

Our repetition of Osaka's experiment was carried out in duplicate and the final measurements which were obtained by the same method of experimentation just quoted are as follows:

	Inverted in concentrated solution.		Inverted in dilute solution.
First experiment.......	—19 65	First experiment.......	—20 25
Second experiment.....	—19 70	Second experiment....	—20.40
	Mean,[1] —19 67		Mean, —20 32

These results fully confirm Osaka's values as to the direction of the rotation difference and its approximate magnitude. Having thus duplicated a typical one of his experiments, we wish to examine his interpretation of them. It is to be observed that in the quoted experiment of Osaka's, 4 cc. of 2.5 N hydrochloric acid were added to each of the flasks containing the solutions to be inverted in dilute solution; on dilution to 25 cc., the acidity was then the same as in the original solution when made to the volume mark. On the other hand, no acid was added to the solution which had been removed from the original solution and to which sodium acetate had been added to stop any further inversion. Its acidity was, therefore, only a fifth of the acidity of the solution which had been diluted without addition of sodium acetate. It is well known that hydrochloric acid increases the levo-rotation of invert sugar solutions,[2] the increase being approximately in proportion to the concentration of acid present, and it seemed possible, therefore, that the difference in rotation of the two sets of solutions might be due to such an influence. The following experiments were accordingly made.

Fifteen (15) cc. of a solution containing 13.445 g. each of pure glucose and fructose in 100 cc. were added to each of four 25 cc. flasks. After addition of hydrochloric acid and sodium acetate as indicated below, the volumes were completed to 25 cc. at 20° and the rotations read in a 200 mm. tube at that temperature in a saccharimeter. The concentration of invert sugar in these solutions was nearly the same as for the solutions employed in our repetition of Osaka's experiment.

(1) One cc of 2.5 N hydrochloric acid, 3.4 g sodium acetate. Rotation —19.0° V.

(2) Five cc of 2 5 N hydrochloric acid, 3 4 g. sodium acetate Rotation —19 0° V

(3) One cc of 2.5 N hydrochloric acid, no sodium acetate. Rotation —16.95° V.

(4) Five cc. of 2.5 N hydrochloric acid, no sodium acetate. Rotation —17.35° V.

[1] These measurements refer to a tube length of 20 cm , and to Ventzke degrees, using white light. If expressed in circular degrees they agree fairly well with Osaka's quoted values, since 100 Ventzke degrees equal about 34.6 circular degrees.

[2] von Lippmann, *Chemie der Zuckerarten*, 1, 922 (1904).

These experiments (3 and 4) confirm the well known influence of the acid concentration on the rotation of invert sugar, but show further (1 and 2) that in the presence of sodium acetate, which neutralizes the acid, the variation in the strength of the latter does not affect the reading. Accordingly, the greater negative rotation, when the sucrose was inverted in dilute solution, cannot be due to the influence of the acid, which had been added in greater amount than when the sugar was inverted in higher concentration.

In Osaka's experiment the portion of original solution inverted in concentrated solution was not removed until the day following the removal of the portion intended for inversion in dilute solution;[1] it, therefore, stood in concentrated solution in the presence of 5 cc. of 2.5 N hydrochloric acid per 25 cc. for one day longer than did the portion intended for inversion in dilute solution. Any destruction of invert sugar (particularly of fructose) by the acid during this period might, therefore, have been different in degree in the portions inverted in concentrated and dilute solution, thus causing their rotations to be different. In order to test this possibility, the following experiments were carried out, the procedure being the same as Osaka's, with the exception that the 5 cc. for inversion in concentrated solution were removed at the same time as the 5 cc. intended for inversion in dilute solution. The procedure of making up the final volume of 25 cc. for the inversions in concentrated and dilute solutions is indicated below. The solutions were kept at 25° and were read in a saccharimeter at 20° as soon as the volumes were completed to 25 cc. For sodium acetate, a solution which contained 2.05 g. of the anhydrous salt in 7 cc. (which was found by trial to be sufficient to stop inversion) was employed.

	Concentrated solution Cc	Dilute solution Cc.
Added on the first day		
Original solution[2]	5	5
Sodium acetate solution	7	0
2 5 N hydrochloric acid	0	4
Water	5	8
	—	—
	17	17
Added further on the second day		
Sodium acetate solution	0	7
Water	8	1
	—	—
	25	25

In addition to an original solution containing 80 g. of sucrose in 100 cc.,

[1] See note 1 on page 1573

[2] It was found necessary for accuracy to weigh the quantity of original solution which was used; these weights are recorded in the second and third columns of the following tables.

three solutions were prepared and tested in the same manner: (*a*) A solution of equal parts of glucose and fructose corresponding to the above sucrose solution; (*b*) a fructose solution of one-half the concentration of the invert sugar solution; (*c*) a glucose solution of one-half the concentration of the invert sugar solution. The results of these experiments, in which portions of the original solutions intended for inversion in concentrated and dilute solution had been removed each day for a number of days in order to determine the effect of the prolonged action of hydrochloric acid on the original solutions, are shown in Tables I–IV.

All of the polarizations were checked by a standardized quartz plate and the rotations are corrected for any change of zero of the instrument during the period of the experiments. The data show that concentrated solutions of inverted sucrose, of invert sugar prepared by mixing pure glucose and fructose, and of fructose, decrease in levorotation progressively

TABLE I—SUCROSE

Date.	Sample weight, dilute inversion G	Sample weight, concentrated inversion. G.	Rotation, dilute.	Rotation, concentrated	Rotation, dilute (cor.) [2]	Rotation, concentrated (cor.).[1]
Jan. 9	6 2150	6 1050	—18 45	—18 20	—18 35	—18 45
10	6 2232	6 2355	—18 20	—18 20	—18 05	—18 05
11	6 2590	6 1890	—17 75	—17 65	—17 55	—17 60
12	6 1050	6 1165	—16 70	—16 80	—16 90	—17 00
13	6 1310	6 1475	—16 30	—16 40	—16 45	—16 50
14	6 1410	6 1550	—15 80	—15 90	—15 90	—15 95
16	6 2695	6 1655	—15 70	—15 35	—15 50	—15 40
17	6 1235	6 1355	—15 00	—15 00	—15 16	—15 10
18	6 2235	6 3440	—15 00	—15 30	—14 90	—14 90

Av........ . 6 1808

TABLE II—INVERT SUGAR.

Date.	Sample weight, dilute inversion. G.	Sample weight, concentrated inversion. G.	Rotation, dilute.	Rotation, concentrated.	Rotation, dilute (cor) [2]	Rotation, concentrated (cor).[2]
Jan 9	6 1600	6 1350	—18 30	—18 35	—18 15	—18 25
10	6 2140	6 2020	—18 00	—18 05	—17 70	—17 75
11	6 0040	6 0065	—16 90	—17 00	—17 20	—17 30
12	6 0960	6.2650	—16.85	—17 40	—16 90	—16.95
13	6 1245	6 1240	—16 55	—16 60	—16 50	—16.55
14	5 9855	6 1165	—16 00	—16 35	—16 35	—16.35
16	6 0610	6 1240	—15 75	—16 00	—15 85	—15.95
17	5 9950	6 0780	—15 30	—15 45	—15 60	—15.55
18	6 0850	6 1620	—15.30	—15 50	—15 35	—15.35

Av... . . 6 1077

[1] Corrected to a uniform sample weight of 6.1808 g. by direct proportion.
[2] Corrected to a uniform sample weight of 6.1077 g. by direct proportion.

TABLE III—GLUCOSE.

Date	Sample weight, dilute inversion G	Sample weight, concentrated inversion G	Rotation, dilute	Rotation, concentrated	Rotation dilute (cor)[1]	Rotation, concentrated (cor)[1]
Jan 9	5 6650	5 6600	+23 15	+23 05	+23 10	+23 05
10	5 6470	5 6550	+23 10	+23 10	+23 15	+23 10
11	5 6640	5 6875	+23 10	+23 15	+23 05	+23 05
12	5 6285	5 6320	+23 00	+22 90	+23 10	+23 00
13	5 6460	5 6810	+23 05	+23 05	+23 10	+22 95
14	5 6630	5 6675	+23 10	+23 05	+23 10	+23 00
16	5 6725	5 6645	+23 10	+23 05	+23 05	+23 00
17	5 6530	5 6560	+23 05	+22 95	+23 05	+22 95
18	5 6395	5 6465	+23 00	+22 95	+23 05	+23 00
Av		5 6571				

TABLE IV—FRUCTOSE

Date	Sample weight, dilute inversion G	Sample weight, concentrated inversion G	Rotation, dilute	Rotation, concentrated	Rotation, dilute (cor)[2]	Rotation concentrated (cor)[2]
Jan 9	5 7000	5 6950	—42 35	—42 25	—42 15	—42 10
10	5 6510	5 6730	—41 60	—41 65	—41 80	—41 65
11	5 6715	5 6600	—41 65	—41 45	—41 65	— 41 55
12	5 6595	5 6890	—41 30	—41 50	—41 40	—41 40
13	5 6695	5 6750	—41 00	—41 00	—41 05	— 41 00
14	5 6955	5 7020	—40 85	—40 95	—40 70	—40 75
16	5 6700	5 6810	—40 50	—40 65	—40 55	—40 60
17	5 6560	5 6135	—40 25	—40 05	—40 40	—40 50
18	5 6870	5 6980	—40 40	—40 55	—40 30	—40 40
Av		5 6748				

with age when hydrochloric acid is present It is evident that the decomposition of fructose by the acid is responsible for the change of rotation, since the solution of glucose in acid retains a constant rotation. It will be recalled that in Osaka's experiment the reading of the solution which was removed on the *first* day and allowed to stand in dilute solution (in which the destruction of fructose is arrested) was —6.594 circular degrees, while that of the solution which was removed on the *second* day and immediately diluted and read was only —6.313. The difference of 0.281°, corresponding to 0.81° Ventzke, is of the same order of magnitude as the average daily loss in rotation recorded in Tables I, II, IV, that is, about 0.35° Ventzke. The somewhat higher value of Osaka's experiment may be due to his working at 25°, whereas our experiments were made at 20°. Our experiments show no certain difference in rotation between sucrose solutions which are inverted in dilute and in concentrated solution, provided the inversions are carried out under comparable conditions. We

[1] Corrected to a uniform sample weight of 5 6571 g by direct proportion
[2] Corrected to a uniform sample weight of 5 6748 g by direct proportion

are forced to discard Osaka's experiments because the inversions in dilute and concentrated solutions were not carried out under comparable conditions. The conclusion from our experiments is that the hydrolysis of sucrose by hydrochloric acid is not to any detectable degree a reversible reaction in aqueous solution.

Repetition of Visser's Experiments.—Visser[1] states that the inversion of sucrose by invertase is not complete as compared with its inversion by acids; a 0.25 N sucrose solution gave, after inversion by invertase, a rotation of —3.26°, while the rotation of a similar solution inverted by a 0.25 N hydrochloric acid was —3.42°. He therefore assumes the existence of an equilibrium in the hydrolysis of sucrose by invertase, which would afford a basis for the belief that this reaction is reversible. In our repetition of Visser's experiments (the rotations of the solutions were read in a saccharimeter and with a tube of different length from that used by Visser), —20.7° and —19.5°, respectively, were obtained for the solutions inverted by hydrochloric acid and invertase; after exactly neutralizing the former with sodium carbonate, to make it really comparable with the latter, which was very slightly acid with acetic, the rotation became —19.6. The difference observed by Visser was, therefore, due to the well known influence of hydrochloric acid on the optical rotation of invert sugar, and does not indicate the existence of an equilibrium in the inversion of sucrose by invertase. Visser also stated that a solution containing equal parts of glucose and fructose, in an amount equivalent to a 0.25 N sucrose solution, gave a rotation of —3.42°, that is, the same as a 0.25 N sucrose solution inverted by hydrochloric acid. As this statement is, however, in full disagreement with the well known influence by hydrochloric acid on the rotation of invert sugar solutions, the experimental data cannot be accepted. A synthesis of sucrose from invert sugar which Visser supposedly obtained is described by him in the following words: "A solution, which contained equal amounts of fructose and glucose, showed an initial rotation of —12.46°; after being subjected to the action of invertase for two months, the rotation was —12.29°." No further details in regard to this experiment are given. The possibility of this supposed reversion was tested by diluting a solution, containing equal amounts of glucose and fructose with a solution of invertase,[2] so that the rotation after dilution was approximately the same as that of a certain quartz plate; the latter was used to control the constancy on the saccharimeter scale of the initial rotation of the solution. After addition of toluene to prevent the growth of microörganisms, the solution was kept in a 200 mm. tube and

[1] *Z. physik Chem.*, 52, 275 (1905).

[2] The invertase solution which was used in these and the other experiments recorded in this article was prepared from yeast by rapid autolysis according to the method described by one of us in the accompanying article.

the rotation at 20° observed at various times during a period of three and a half months. All of the readings lay between the values —50.65 and —50 70, as compared with the reading of the quartz plate, which was —50.15. There was accordingly no change in rotation beyond the limits of experimental error and no synthesis of sucrose was detected

As an indication of the activity of the invertase present in this solution, it may be stated that a sucrose solution of equivalent concentration and containing the same amount of invertase was half inverted in one and one-half days at 20°. This experiment was better controlled, we believe, than was Visser's and no indication of a synthesis of sucrose by the action of invertase was found

Kohl's Experiment —F G Kohl[1] has stated that "yeast extracts with a high inverting power, when acting on sucrose solutions of known concentration in the absence of light and at different temperatures, produced glucose and fructose up to certain limits and then remained stationary or brought about a reversion." This supposed reversion was tested as follows, the degree of acidity being varied by adding acetic acid and sodium phosphate to the solutions in view of the possibility that the acidity may play an important part in reversion Five 200 mm. observation tubes were prepared so that each one contained a synthetic invert sugar solution (equal amounts of glucose and fructose) of the same strength and a small amount of potassium fluoride to prevent the growth of micro-organisms, the concentration of these invert sugar solutions was 10 g per 100 cc The hydrogen ion concentrations were 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9}, respectively,[2] or, in other words, the first two solutions were slightly acid, the third was approximately neutral, and the last two were slightly alkaline The invertase used was quite active, when diluted 1 to 11, it inverted a 0 5% sucrose solution to the extent of 50% in 5 minutes at 30° The dilution of this invertase in the above sugar solutions was 3 to 40 All the solutions were kept in the dark during the experiment. The data, as indicated in Table V, do not give evidence of any reversion of invert sugar to sucrose

TABLE V —TEMPERATURE 20°

Date.	10^{-5}H+	10^{-6}	10^{-7}	10^{-8}	10^{-9}	Quartz plate
Dec 15	—12 35	—12 40	—12 35	—12 35	—12 35	—50 15
19	—12 35	—12 40	—12 35	—12 35	—12 35	—50 15
22	—12 35	—12 35	—12 35	—12 30	—12 35	—50 15
Jan 4	—12 35	—12 40	—12 30	—12 35	—12 35	—50 15
10	—12 40	—12 45	—12 35	—12 40	—12 40	—50 15
28	—12 35	—12 35	—12 30	—12 35	—12 40	—50 15
Mar 23	—12 40	—12 35	—12 35	—12 35	—12 40	—50 15

[1] *Bot Centrbl*, *Beihefte*, *Abt I*, 23, 64f-640, Jan 10, 1908
[2] Cf A A Noyes, THIS JOURNAL, 32, 823 (1910), for the preparation of solutions with these hydrogen ion concentrations

Pantanelli's Experiments.—In 1906, Pantanelli[1] published a number of experiments on the inversion of sucrose by aqueous extracts of the mold *Mucor mucedo*. Among them are three instances in which the power of an invert sugar solution to reduce alkaline copper solutions decreased when the solution was mixed with the extract of the mold. Without making thorough inquiry into the cause of these decreases, Pantanelli drew the conclusion that they indicate a reversion of the invert sugar, the extent of the reversion being as high as 24% in one of the experiments. The evidence from this·work for a synthesis of sucrose from invert sugar is slight, because the experiments were not checked by polarimetric data or the other usual ways for detecting the presence of sucrose, nor were the various possible sources of uncertainty controlled. No confirmation of this reversion has been subsequently published, although it should not be difficult to crystallize sucrose from the solutions if such an extensive synthesis as Pantanelli's experiments indicate were really to be obtained. We have not tried to duplicate Pantanelli's rather doubtful observations upon the action of invertase which may be prepared from *Mucor mucedo*, as our work has been limited to the invertase which is obtained from yeast.

Summary.

A solution of the enzyme invertase which was prepared by the rapid autolysis of yeast under the influence of toluene, and purified by clarification with neutral lead acetate and hydrogen sulfide, and by subsequent dialysis, was allowed to act upon aqueous invert sugar solutions, which were maintained at various degrees of slight alkalinity and acidity, in an attempt to detect a possible synthesis of sucrose by the enzyme.

Although numerous experiments under various conditions were tried, not one showed any indication of such a synthesis. A repetition of Osaka's experiments, which indicate the synthesis of sucrose from invert sugar in concentrated solution, in the presence of hydrochloric acid, shows that the change of polariscopic rotation which he observed is not due to synthesis, but is caused by the decomposing action of the acid upon fructose.

A repetition of similar experiments by Visser shows that his supposed synthesis of sucrose was only a change in rotation which is caused by the well known influence of hydrochloric acid upon the rotatory power of fructose.

An examination of the experiments of Kohl and of Pantanelli on the synthesis of sucrose by the action of invertase upon invert sugar solutions, shows the experimental evidence to be very doubtful.

Our conclusion, from a consideration of the experiments of others and from our own data is that invertase from yeast accomplishes a complete hydrolysis of sucrose to yield invert sugar and that the reaction does not

[1] *Atti della R. Accad. dei Lincei*, **15**, first semester, 587–94 (1906).

establish a mobile equilibrium, and is not a reversible or balanced reaction, within our limits of detection.

BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

NEW BOOKS.

The Progress of Scientific Chemistry. By SIR WILLIAM A TILDEN Second Edition. 360 pp. Longmans, Green & Co. 1913. $2.25

The merited success of the first edition of this work, published in 1899, has justified the present revised edition in which several new subjects, such as radiochemistry, are included. The majority of the chapters are written from a somewhat old-fashioned standpoint, but are readable and stimulating. The biographical notes and references appended to the several chapters add to the value of the work.   GILBERT N. LEWIS.

Chemistry and Its Borderland. By ALFRED W STEWART. Longmans, Green & Company. 314 pp Price, $1.50, net.

This is a very readable and instructive general description of a number of selected topics of recent physical and chemical research. It includes chapters on such topics as the Relations between Chemists and Industry, Chemical problems of the Present and Future. Organization of Chemical Research (in England), The Methods of Chemical Research, etc. Separate chapters are devoted to the discoveries by means of the spectroscope, stereochemistry, colloids, the inert gases of the atmosphere, radium, niton, transmutation of the elements, the nature of the elements, etc. The author is evidently following closely the work of the English school of chemists, and does not hesitate to accept for niton all the properties ever ascribed to it. He does not doubt the transmutation of copper into lithium, as published by Ramsay and Cameron. Madam Curie's described inability to repeat this transmutation is "negative evidence that can hardly outweigh the positive." A bold author makes better reading than an apologetic one, and we do not refer to these facts in critical mood. This kind of book is greatly needed to help keep a very large class of chemists up-to-date and to inspire the aspiring younger generation. It is also very readable to the "near scientist." The author's treatment of his subject reminds one of R. K. Duncan's very interesting and instructive publications.

The author has occasionally fallen into a common didactic error. In this way he has given some impressions which, while they may represent desirable conditions of research, give too much credit to the foresight of chemists and not enough to the utility of their powers of observation. Bacon credited Herodotus with the statement that the Egyptians who deified discoverers, worshipped more animals than men, because the former made most of the discoveries. So also it is still true that many discoveries

are made and then later realized, and that discovery to order and from the minute" is rare. An interesting case is the author's description of the commercial fixation of atmospheric nitrogen. Of course, he knew how the facts were discovered, but to read his description one might be led to believe that the invention consisted first in finding, by search, the cheapest supply of nitrogen. This was found in the air. This had to be combined with some other cheap reagent. Oxygen was found to be the next cheapest element, so he chose oxygen, and then he had to find some means of combining them. High temperature was known to produce such reaction, and as an electric arc,[1] was a source of high temperature, it was chosen, etc., etc. None of this conveyed impression of aim and end corresponds with the facts. It was discovered, without any preconception or purposeful plan, that an arc produced the combination of the gases of the air, and the reaction was then studied. The important lesson comes to us, in the reviewer's mind, from the fact that quantitative investigation of details of the discovery is what has led to the possibility of its technical application. This investigating spirit it doubtless was, which created for us such chemists as Priestley and Cavendish, to whose observations the present, now logical manufacture of nitric acid from the air is due.

The final chapter deals with chemical research in England, and the present and desirable methods of its encouragement there. The cry is "more money," or endowments, in order to make easier the way of the research chemist. This is also frequently the cry in this country. In both lands the prevailing opinion is that chemists are too poorly paid, that the country's advance would be more rapid if there were more and better paid chemists. Barring the fact that corresponding opinions are held by the clergy, the doctors and lawyers, the masons and the steam fitters of both countries, the contentions are probably true, and Huxley was right when he said, "A Watt, Davy or Faraday is cheap at a hundred thousand pounds." Many authors of note, from Bacon down, have taken the view held by the author. Some of the splendid work now being done by English research men is directly traceable to the present good, but admittedly inadequate methods of encouraging research. Possibly governments, seeing the results of such experiments carried on for years, as is already the case in England, will recognize the value to the country as a whole of increasing its yield of research chemists. The book should help this desirable end, by presenting in readable form, the many accomplishments of pure research in chemistry and its borderland.

<div align="right">W. R. Whitney.</div>

Qualitative Chemical Analysis. By W W Scott, A M D Van Nostrand Co., New York.

The contents of this book are carefully and excellently divided into parts.

The relation between qualitative and quantitative analysis has been clearly brought out. This point, which is very important, is usually lacking in the smaller text books.

The first part contains a very concise description of the physical chemical side of qualitative analysis. One of the characteristics throughout the book is its conciseness. A very large amount of material is contained in a small quantity of print.

There are abundant notes and precautions, which are valuable to the student, distributed through the text. Another pleasing point is the alternative methods that are offered.

Part II contains the bases. Part III gives the analysis of the acids, while the systematic analysis of a substance is given under Part IV. Part V is devoted to tables of reactions.

Perhaps some might desire a little more with regard to the characteristic compounds. However, one must realize that a lot of information is contained in the tables of reactions forming the last part.

To many the absence of equations may prove a weak point.

The use of an arrow, beside a compound, pointing downwards is usually supposed, to indicate a precipitate. In this text it is also used to show substances that are almost unionized.

The book contains some errors, that should be corrected, such as thallium being precipitated as $TlCl_3$, the statement that there are no rare elements belonging to the ammonium carbonate group, etc.   C. JAMES.

Laboratory Manual of Glass-Blowing. By FRANCIS C. FRARY. McGraw-Hill Book Company. 1914. Pp. vi + 60   Price, 75 cents

This welcome little manual provides a clear and detailed discussion of the elementary processes of glass-blowing. Much delay is spared and some expense avoided, if some one in the laboratory can seal on a new stopcock or join two tubes by fusion, or fit together a hard and a soft glass tube by ground joints. Such manipulation is well described here, fully and clearly, so that a beginner may be sure of knowing what to do, even if the knowing what to do must be supplemented by hours of practice. The author, whose conception of the proper content of such a manual seems well considered, avoids the description of processes which the amateur cannot be advised to undertake. The reviewer takes a very special pleasure in commending the little book to all who have to use glass apparatus more complicated than beakers and funnels.   EDWARD W. MORLEY.

Biochemic Drug Assay Methods. With special reference to the pharmacodynamic action of drugs By PAUL S. PITTENGER, Instructor in Pharmacodynamics, Department of Pharmacy and Chemistry, Medico-Chirurgical College, Philadelphia. 158 pp   Price, $1.50. P. Blakiston's Son & Company. Philadelphia.

This manual, the first to be published which takes up this important subject, is a reflection of the interest of physicians and pharmacists in

drugs of standard and uniform potency but, in spite of the title, only physiological assay methods are discussed. The author has given a fair amount of the methods and operative technic commonly advocated for the physiological assay of the digitalis group, ergot, epinephrin, pituitary gland, cannabis indica, etc. In addition there is offered some elementary, and, to a degree, very unsatisfactory pharmacology. The manual does not provide adequate knowledge for the training of pharmacists in physiological assay and is too elementary for use by medical students. It may, however, find some use in giving pharmacy students, and others interested in the subject, a reasonable knowledge of physiological assay methods without the necessity of studying pharmacology and pharmacological methods more in detail.   WORTH HALE.

Kinetische Stereochemie der Kohlenstoffverbindungen. VON DR ARTHUR VON WEIN
BERG   Pp VIII + 107   25 figures   Friedr Vieweg & Sohn Braunschweig
1914   Price, M 3, paper, M 4, cloth

It is a well-known fact that ordinary structural and stereochemical formulas take no account of possible intramolecular motions of atoms. The author of this book introduces certain assumptions with regard to rotating and vibrating atomic motions, and applies these to heats of combustion and molecular refractions in connection with various reactions and compounds.

Single bonded atoms are assumed to rotate or swing around an axis, double and triple bonded atoms to vibrate. With heats of combustion, atomic constants are derived which when added, agree very well with the experimentally found values for many substances. These constants, however, must be modified for different classes of compounds, and these changes are pictured as dependent upon the rotational or vibrational motions of the combinations. The volumes occupied by atoms are based upon the molecular refractions. Starting with Eisenlohr's atomic refraction values for single bonded atoms, making certain assumptions with regard to the rotational and vibrational motions of double and triple bonded atoms in connection with the volumes occupied by them, values for the atomic refractions of the latter are deduced which agree with those determined experimentally. The constants so obtained and the principles developed are then applied to the interference of double bonds, aromatic and nonaromatic ring structures, quinones, desmotropy, alloisomerism, color theory, and the asymmetric carbon atom.

Some interesting views are developed in this book, but it may be questioned whether the assumptions used are based upon satisfactory underlying principles. However, a picture is developed of some of the possible ways in which the motions of atoms within molecules may play their part in chemical phenomena.   K. G. FALK.

THE JOURNAL

American Chemical Society

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(Founded by Ira Remsen)

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1915.

By F. W. CLARKE, T. E. THORPE, W. OSTWALD AND G. URBAIN.

The Council of the International Association of Chemical Societies, with which the Committee on Atomic Weights is now affiliated, recommended, at its meeting in September, 1913, that the annual report of said committee should be published in August. The present report, therefore, is submitted in compliance with that recommendation, although delays due to the difficulties of correspondence may sometimes prevent simultaneous publication in all countries.

Since the report for 1914 was prepared, a number of new atomic weight determinations have been published. These may be briefly summarized as follows:

Silver, Sulfur and Chlorine.—Scheuer[1] dissolved pure silver in sulfuric acid and collected and weighed the sulfur dioxide given off. The weighed sulfate was then converted into chloride by heating in a current of gaseous hydrochloric acid. Three ratios were thus determined, which gave the three desired atomic weights independent of all former determinations. The results obtained are: Ag = 107.884, S = 32.067, Cl = 35.460. The value for silver is rather high; the other values agree with those generally accepted.

[1] *Arch. sci. phys. nat.*, [4] 36, 381.

Calcium.—Oechsner de Coninck[1] has determined the atomic weight of calcium by conversion of the carbonate into the sulphate. This final value is Ca = 40.13.

Barium.—Also redetermined by Oechsner de Coninck.[2] Barium carbonate was dissolved in nitric acid and the carbon dioxide so evolved was weighed. The value found was Ba = 137.36.

Copper.—Atomic weight determined by O. de Coninck and Ducelliez.[3] Copper was oxidized by nitric acid and the oxide was weighed. In five experiments they found Cu = 63.523 to 63.605; in mean, 63.549. These atomic weight determinations by O. de Coninck are published in the briefest possible way, without any of the details that are commonly regarded as essential. How were the substances purified? Were the weights reduced to a vacuum?

Cadmium.—Quinn and Hulett[4] have redetermined the atomic weight of cadmium by electrolysis of the chloride and bromide. In each series the cadmium was collected and weighed in mercury. From the chloride, with Cl = 35.458, Cd = 112.32. From the bromide, with Br = 79.92, Cd = 112.26. These values agree well with those previously found by Perdue and Hulett and by Laird and Hulett, but are much lower than the value (Baxter's) adopted in the table. The cause of the difference is yet to be satisfactorily explained; but it must be due to a constant error in one or the other of the methods employed. A change in the table would, be premature.

Mercury.—Taylor and Hulett[5] prepared mercuric oxide by heating pure mercury in oxygen. Weighed amounts of the oxide were then decomposed by heating it with metallic iron, and the mercury was collected and weighed. From the data thus obtained Hg = 200.37. This, as in the case of cadmium, is lower than the recognized value, and its acceptance or rejection must await farther evidence.

Vanadium.—Atomic weight redetermined by Briscoe and Little,[6] from analyses of the oxychloride $VOCl_3$. The mean value found was V = 50.950, but 50.96 is preferred.

Selenium.—Jannek and Meyer[7] determined the atomic weight of selenium by oxidizing Se to SeO_2. The mean of ten experiments gave Se = 79.140.

The same constant was deduced by Bruylants and Bytebier[8] from the

[1] *Bull. acad. belg.*, 1913, 222.
[2] *Rev. gén. chim.*, 16, 245.
[3] *Ibid.*, 16, 122.
[4] *J. Physic. Chem.*, 17, 780.
[5] *Ibid.*, 17, 755.
[6] *J. Chem. Soc.*, 105, 1310.
[7] *Z. anorg. Chem.*, 83, 51.
[8] *Bull. acad. belg.*, 1912, 856. According to Germann (*Compt. rend.*, 157, 926), the normal liter of oxygen weighs 1.42900 g.

density of selenium hydride, SeH_2. In four series of experiments the weight of a liter of the gas at 0° and 760 mm. was found to be 3.6715 g. For the weight of a liter of oxygen under the same conditions they found 1.4295 g. By the method of limiting densities and with H = 1.008, Se = 79.18, which is near the value given in the table.

INTERNATIONAL ATOMIC WEIGHTS, 1915.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39 88	Neon	Ne	20 2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorine	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150 4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79 2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23 00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulfur	S	32.07
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

Tellurium.—Dennis and Anderson[1] purified tellurium by preparing the hydride TeH_2 from aluminum telluride, and condensing the gas to a solid at the temperature of liquid air. From the hydride the metal was obtained by heating to $500°$. Thirty-one conversions of Te thus prepared into TeO_2 gave in mean Te $= 127.6$. Other determinations by a volumetric method gave a lower value, near 127.50. The authors conclude that the higher, hypothetical "dvitellurium" does not exist.

Scandium.—Lukens[2] prepared scandium oxide from Colorado wolfram. By calcination of the sulfate to oxide they found Sc $= 44.59$ and 44.77. The material was probably not quite pure.

Yttrium.—Meyer and Weinheber,[3] by conversion of yttrium oxide into sulfate, found Yt $= 88.75$. By the reverse process they found Yt $= 88.74$. Corrected to a vacuum, this becomes 88.70.

Ytterbium and Lutecium.—Atomic weights reinvestigated by Auer von Welsbach.[4] For ytterbium (aldebaranium) he found Yb $= 173.00$. For lutecium (cassiopeium), Lu $= 175.00$. (See note.)

Iridium.—Holzmann[5] made four reductions of the salt $(NH_4)_2IrCl_6$ in hydrogen, and found Ir $= 193.42$. This is higher than the accepted value and not conclusive enough to justify a change.

Helium.—Heuse,[6] in seven determinations of the density of helium, finds the weight of a normal liter to be 0.17856 g. Hence, by the method of limiting densities, He $= 4.002$.

Neon.—From two determinations of the density of neon, Leduc[7] finds Ne $= 20$, when H $= 1$.

No changes of serious importance seem to be needed in the atomic weight table. Possibly the values for yttrium, ytterbium, helium and neon should be changed, but such action may well be deferred until next year. Some experiments by Richards and Cox[8] on the purity of lithium perchlorate also suggest a possible lowering of the atomic weight of silver, namely, from 107.88 to 107.871.

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F. W. CLARKE,
T. E. THORPE,
W. OSTWALD,
G. URBAIN.

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NOTE.—Since this report was finished and approved, Professor Urbain has informed me that, jointly with M. Blumenfeld, he has redetermined

[1] THIS JOURNAL, 36, 882.
[2] *Ibid.*, 35, 1470.
[3] *Ber.*, 46, 2672.
[4] *Monatsh. Chem.*, 34, 1713.
[5] *Sitzungsb. phys.-med. Soc. Erlangen*, 44, 84.
[6] *Verh. Deutsch. physik. Ges.*, 15, 518.
[7] *Compt. rend.*, 158, 864.
[8] THIS JOURNAL, 36, 819.

the atomic weight of neo-ytterbium with great care. The earth was subjected to many fractionations, and each fraction was studied magnetically and spectroscopically. The value found for the atomic weight, the mean of 13 determinations, was 173.50. He suspects that the "aldebaranium" studied by Auer von Welsbach contained an element of lower atomic weight, probably thulium. Urbain's paper will be published in the near future, perhaps before this report appears.   F. W. C.

STUDIES IN CONDUCTIVITY. II. THE CONDUCTIVITY OF SOME FORMATES AND OF HYDROGEN CHLORIDE IN (ANHYDROUS) FORMIC ACID. CASES OF APPARENT AGREEMENT OF STRONG ELECTROLYTES WITH THE MASS LAW.[1]

BY H. I. SCHLESINGER AND A. W. MARTIN.[2]
Received May 12, 1914.

In the first paper of this series, Schlesinger and Calvert[3] showed that the solutions formed when ammonia is passed into formic acid are excellent conductors and that the electrolyte, ammonium formate, obeys the law of mass action, although it is highly ionized. It is well known that strong electrolytes do not, in general, obey this law and these solutions, therefore, are exceptionally interesting. Consequently, we have undertaken to extend this work, with the intention of determining the limiting concentrations within which the law is applicable and of obtaining results of greater accuracy by improving the methods employed. In addition to a study of the conductivity of these solutions, their viscosity was also determined. Since it was possible that the agreement with the mass law in the one case, ammonium formate, might be due to a cancellation of deviations from the law in opposite directions, the validity of the conclusion that the agreement is not accidental in character was tested by studying the behavior of other formates in this solvent. Finally, preliminary determinations of the conductivities and freezing points of solutions of hydrogen chloride in the same solvent were carried out, as there was reason to believe that previous work on this subject by Zanninovich-Tessarin[4] was incorrect.

The formic acid used in this work was purified by a method which is a considerable improvement over that employed by Schlesinger and Cal-

[3] THIS JOURNAL, 33, 1924 (1911).

[4] Z. phys. Chem., 19, 251 (1896).

vert.[1] They distilled from phosphorus pentoxide, under reduced pressure. While this method yields an acid of fair quality, it is accompanied by considerable decomposition and loss of material and requires a large amount of time, since the distillation has to be repeated from five to ten times to obtain good results. An effort was made to improve this method by carrying out the distillation at still lower pressure, but the results were not much better. Attempts were also made to produce the anhydrous acid directly by heating anhydrous sodium formate mixed with acid salts, such as acid potassium sulfate, in the dry condition as well as in solution in anhydrous formic acid, but these methods gave neither good yields nor good products.[2] The method finally determined upon was distillation of the acid from boric anhydride. The anhydride was prepared by heating boric acid to a high temperature in a furnace until all bubbling and foaming ceased. The resulting melt was poured on an iron plate and allowed to cool in a desiccator. The glassy boric anhydride was then powdered and introduced directly into the formic acid,[3] with which it was allowed to remain in contact for several days. After a few days the powdered material sets into a hard mass, from which the supernatant liquid can be distilled at reduced pressure without bumping. The distillation was carried out in a specially designed apparatus at a pressure of about 12 to 18 mm. and a temperature of about 22° to 25°.

The apparatus used for this distillation is shown in the accompanying sketch (Fig. 1). It was designed to avoid contact of the acid with rubber,
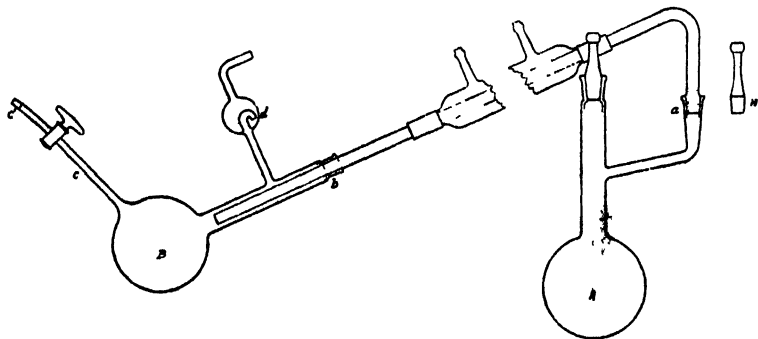
Fig. 1.

for it was soon found that the presence of the latter decidedly affected the quality of the acid. A, in Fig. 1, is the distilling flask which is connected

[1] *Loc. cit.*

[2] See *Chem. Zentr.*, 1907, I, 1470; 1908, I, 998.

[3] The formic acid was especially prepared for this work by Baker & Adamson and originally had a conductivity of about 12–15 × 10^{-5} reciprocal ohms.

with the inner tube of the condenser by the ground joint a.[1] Into the vertical portion of the side neck of this flask, thoroughly washed and dried glass wool was placed to prevent spattering over of the liquid. B is the receiving vessel which is connected with the inner tube of the condenser by means of the ground joint b. In order to empty the receiving vessel after the distillation, it was rotated about the joint b, until the delivery tube c pointed directly downward. The end of this tube is ground to fit into a storage bottle which is shown in the next figure. In this way, the acid could be removed into the vessels in which it was to be used without opening the distillation apparatus or exposing the liquid to air. The tube c was always washed out by a little of the acid before the latter was collected. Before the acid was distilled it was allowed to stand for several days with boric anhydride. From this it was poured into the distilling flask which had been previously charged with a fresh portion of the anhydride. After standing for several days in the apparatus, the distillation was begun by simply reducing the pressure. About one-fifth of the acid (about 50 cc.) distilled off before the liquid had cooled sufficiently to stop the distillation. While this was going on the condenser was cooled with ice water and the receiving vessel with ice. When the distillation stopped, as a result of the cooling of the contents of the distilling flask, the contents of the receiver were warmed and the acid therein collected distilled through a second condenser into a second receiving vessel. The second condenser and receiving vessel were connected with the first by rubber through tubulus d. This procedure had the advantage of washing the apparatus[2] with formic acid before collecting the portion to be used, as well as of subjecting the acid to a partial fractionation. The second receiver also is useful in catching the small amounts of acid which are not condensed in the first. After the first acid condensed had thus been again distilled away, the first receiver was again cooled and the distilling flask warmed to about room temperature. About one-fifth of the original volume of the acid was allowed to remain in the distilling flask at the close of the operation. This, however, together with that collected in the second receiver and that retained by the anhydride,[3] was again treated with anhydride and mixed with fresh portions of acid and redistilled.

While the above seems like a complicated process, it really is not, for, by keeping acid continually drying over the anhydride, a fresh supply can always be obtained in about an hour's time. Occasionally the acid was distilled twice, but no improvement was noted. The acid thus obtained

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[1] "H" is a stopper fitting the flask at "a."

[2] The apparatus was, of course, thoroughly washed occasionally, but better results were obtained if the apparatus was opened as seldom as possible. Before each filling, however, dry air was drawn through the whole apparatus for about half an hour.

[3] The boric anhydride seems to form an unstable, crystalline(?) compound with the acid from which the latter can be recovered by heating.

had an average conductivity of about 6.35×10^{-6}, although occasionally an acid having a conductivity as high as 6.6×10^{-6} reciprocal ohms was obtained. The best acid had a conductivity of 6.2×10^{-6}. Practically no acid was used having a conductivity higher than 6.4×10^{-6}, except for the hydrochloric acid work, in which the greatest accuracy was not sought, and for a few of the concentrated solutions where the conductivity of the solvent was practically negligible, as was proved by trial. The acid used by Schlesinger and Calvert had a conductivity of about 6.8×10^{-6}, so that the present method gives a materially better acid, in addition to giving better yields[1] and requiring less time than did the old method.[2]

Two methods were employed for making up the solutions for the conductivity measurements. Each of the concentrated solutions was made up separately, in the manner described below, and was introduced into the cell described by Schlesinger and Calvert. For the dilute solutions, the dilution method was employed and the special cell F[3] shown in Fig. 2 was used. In this figure is also shown the storage bottle S. It will be seen that by means of the gound joint c'' this bottle can be connected to the receiving flask of the distillation apparatus at c' and, in this way, the conductivity of the acid measured without exposing it to moisture, since the storage bottle is fitted with electrodes ee.[4] This same grinding, c'', fits one of the two-way pipets p shown in the figure. By means of this the acid can be introduced from the bottle into the flask for making up the solution, or into the conductivity cell without exposure to air. In making up the solution, the solute to be used was first weighed[5] out into a thoroughly dried calibrated 25 cc. flask and the flask filled with formic

[1] The anhydride causes only a very slight decomposition of the acid, as is shown by the slight pressure which is developed in flask when the acid has been standing for some days in contact with the anhydride.

[2] Even the conductivity of the best acid, 6.2×10^{-6} seems very large when compared to other pure solvents. It must be remembered, however, that formic acid is quite unusual in that it is not only a good ionizing medium, but is itself fairly highly dissociated when dissolved in other ionizing media. We have thus far not been able to reduce the conductivity of the acid below the values stated although we have subjected the best acid to freezing, etc. However, there is some evidence pointing to a somewhat lower value for the conductivity of pure acid (see p. 1598) and experiments are under way to obtain a better acid by freezing the acid purified in the manner described above. Thus far the improvement has been very small.

[3] This cell is referred to in the paper as cell No 2.

[4] When the acid stands above a certain level the cell constant of the storage bottle is no longer affected by the amount of acid contained in the bottle. When the bottle is full the conductivity of the acid can, therefore, be measured with great accuracy. At lower levels a number of cell constant values were determined and by using a suitable one the conductivity of any acid in the bottle can be determined with sufficient accuracy. It was found, however, that the acid could be kept in the bottle for days without undergoing noticeable change.

[5] Weights were reduced to vacuum when necessary.
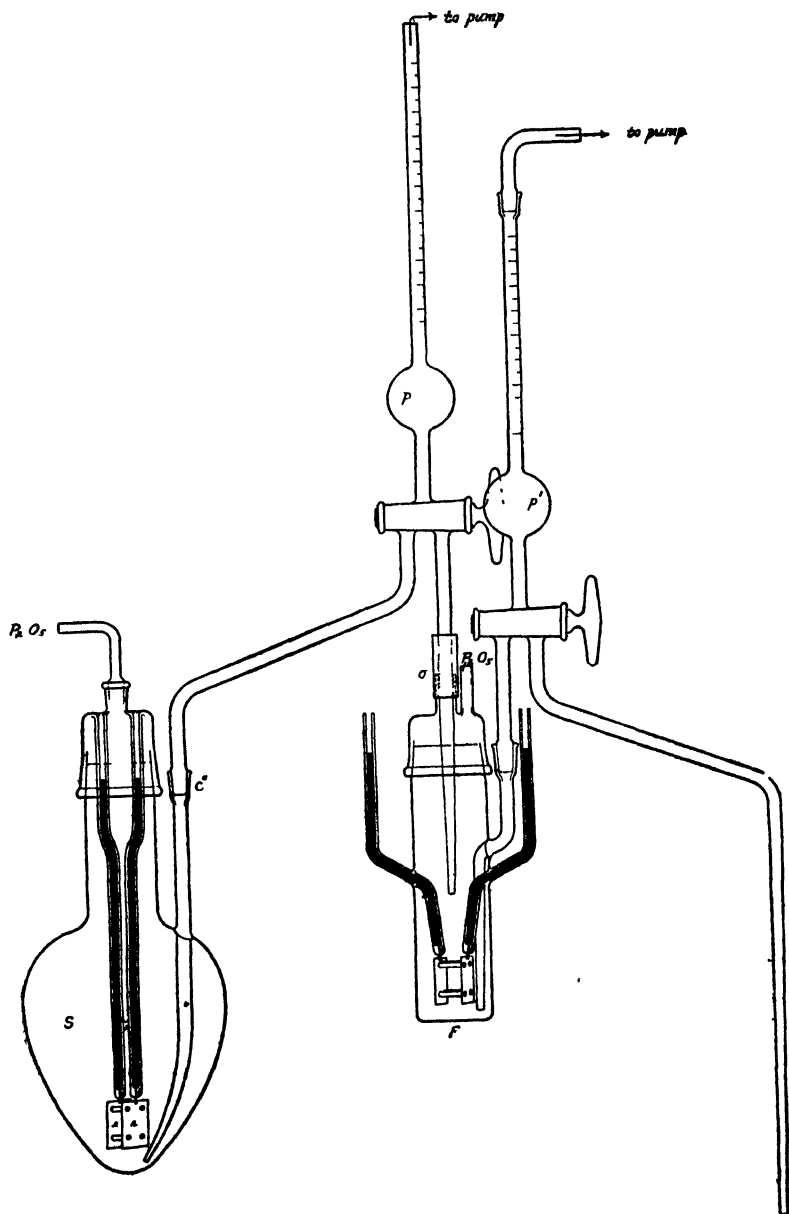
Fig. 2.

acid almost to the mark, by means of the pipet just mentioned. The mixture was thoroughly shaken and then placed in the constant temperature bath. When sufficient time had elapsed for temperature equilibrium to be attained, the acid was filled in up to the mark from the same pipet and the contents again shaken. While not in use, the exposed end of the pipet was protected from moisture by means of a test tube and stopper and the acid remaining in the tip of the pipet was always discarded. From the 25 cc. flask the solution was transferred to the conductivity vessel by means of a pipet, p'', similar to those shown in the figure but of twice their volume. By the use of these pipets all of these steps could be carried out with practically no exposure to moisture.

As stated, the dilution method was employed for the dilute solutions. In these cases the apparatus was set up as shown in Fig. 2 and will need no further description. Pipet p delivers into the cell exactly as much liquid as pipet p' withdraws. Pipet p'' which was used to place the original portion of solution into the cell, delivers just twice as much as does p. The amounts were respectively, 10.02 and 20.04 cc.[1] The procedure of making the dilution measurements is as follows: As described, 20.04 cc. of solution are placed into the cell by means of pipet p'' through the opening o. The pipet is then quickly withdrawn and the apparatus set up as shown in Fig. 2 and placed into the bath. This takes only a little over a minute. From now on exposure to air is avoided and it has been found that solutions[2] in the cell remain unchanged for many hours. After the solution has attained the temperature of the bath $(25° ± 0.01)$[3] a conductivity measurement is made. Then 10 cc. are withdrawn from the cell by means of pipet p' and the stopcock of the pipet turned so as to disconnect the upper portion from the cell. The material withdrawn is run out of the other end of the pipet and the pipet washed with water. Of course, the stem of the pipet which enters into the cell is not allowed to become moist. When the washings are no longer acid the pipet is thoroughly dried by drawing hot, dry air through it. In the meantime, 10 cc. of pure solvent have been transferred from the storage bottle into the cell. The added pure solvent is now thoroughly mixed with the residual solution in the cell by repeatedly drawing the mixture into the withdrawal pipet up to the stopcock and allowing the withdrawn liquid to flow back into the cell. This process is repeated about fifty times, which

[1] The discharge from these pipets is astonishingly regular, being fully as reliable as that of ordinary pipets. By means of the stopcocks the flow can be excellently regulated and the liquid can be very easily drawn to the mark. For convenience, the upper portion of the pipets was graduated instead of having but one mark. The liquid was drawn into the pipets by means of a pump connected through phosphorus pentoxide tubes.

[2] Except for the aniline solutions. See p. 1614.

[3] Hydrogen scale.

takes about five minutes. The conductivity is then measured and the stirring repeated until constant values for the resistance of the solution are obtained. By setting up the apparatus suitably, all of these processes can be made almost automatic and very good results can be obtained. That the method of stirring is efficient and that no losses of solution occur in the stopcocks was tested by making a series of measurements with aqueous solutions of potassium chloride. The agreement with the known values for this salt was excellent. Usually this method of making up the various solutions was employed only for the dilute solutions. As these solutions gave somewhat peculiar results, one or two sets were also made with more concentrated solutions and the results agreed very well with the data obtained from independently made up solutions. Furthermore, these peculiar results were obtained also by Schlesinger and Calvert, whose apparatus was somewhat different, and have received a very satisfactory explanation.

The resistances of the solutions were measured by the Wheatstone-Kohlrausch method, using the small high frequency machine with appropriate capacities in the circuit as described by Washburn and Bell.[1] The roller bridge employed was calibrated, as were also all of the resistances. As no very high resistances were measured it was found unnecessary to use the capacity free resistances described in the paper referred to above. All resistances were measured to within 0.1% which is an accuracy great enough in view of the other possible errors when one is dealing with a solvent like formic acid.

In the following are given the results of the conductivity measurements for solutions of sodium, potassium, ammonium and phenyl ammonium formates and for hydrogen chloride. A number of other data have also been determined, as will appear in the discussion.

Sodium Formate.

The sodium formate used was Kahlbaum's best grade, which gave an analysis corresponding to the anhydrous salt. Before it was used, it was kept for several months in a desiccator with phosphorus pentoxide. Table I gives the results of the conductivity measurements and some calculations based upon them.

Column 1 of the table gives the number of the experiment. The numbers 1, to 5, refer to a series made by the dilution method in cell number 2 as described above; the other data are from entirely independent determinations. Column 2 gives the concentrations, c, in gram molecules per liter; Column 3, the observed specific conductivities, χ, in reciprocal ohms; Column 4, χ_a the observed specific conductivity minus the conductivity of the solvent; Columns 5 and 6 the value $100/equivalent\ conductivity$,

[1] THIS JOURNAL, 35, 177 (1913).

as calculated from the concentration and the specific conductivities given in Columns 3 and 4, respectively. From these values of 100/*equivalent conductivity*, the equivalent conductivity λ can readily be ascertained. The value 100/λ is extensively used in the discussion of the results, and it is for this reason that it was included in the tables rather than the more commonly employed equivalent conductivities themselves The other data in the table will be discussed below

TABLE I —CONDUCTIVITY OF NaOCHO AT 25°.

No	c	x	x_a	100/λ	100/λa	α	$α_a$[1]	K	K_a[1]
0	0			1 500	1 530				
5ₛ	0 00548	0 0003896	0 0003193	1 428	1 715				
4ₛ	0 01095	7457	6814	1 469	1 607				
3ₛ	0 02190	0 001445	0 001381	1 516	1 586				
2ₛ	0 04381	2789	2724	1 571	1 608	0.955	0 951	0 884	0 816
8	0 06670	4115	4052	1 621	1 646	0 925	0 930	0 766	0 817
1ₛ	0 08763	5279	5215	1 660	1 680	0 904	0 910	0 742	0 814
1	0 1046	6197	6129	1 688	1 707	0 889	0 896	0 742	0 811
7	0 1484	8439	8376	1 758	1 772	0 853	0 864	0 735	0 812
9	0 1718	9606	9544	1 788	1 800	0 839	0 850	0 751	0 827
4	0 2043	0 01112	0 01106	1 837	1 847	0 817	0 828	0 742	0 815
6	0 2351	0 01252	0 01245	1 878	1 887	0 799	0 811	0 745	0 816
3ₐ	0 2760	0 01429	0 01423	1 931	1 940	0 777	0 789	0 746	0.816
13	0 2974	0 01517	0 01511	1 960	1 969	0 765	0 777	0 742	0 805
11	0 3338	0 01661	0 01655	2 010	2 017	0 746	0 758	0 733	0 795
14	0 3968	0 01902	0 01896	2 086	2 093	0 719	0 731	0 730	0 788
2²	0 4500	0 02096	0 02089	2 147	2 154	0 699	0 710	0 729	0 784
15	0 5157	0 02304	0 02298	2 238	2 244	0 670	0 682	0 703	0 753
12	0 5933	0 02546	0 02539	2 3305	2 336	0 644	0 655	0 690	0 737
16	0 9867	0 03440	0 03433	2 871	2 877	0 522	0 532	0 564	0 596

As has been recently pointed out by Kraus and Bray[2] conductivity data can be very conveniently examined by a graphical method in order to determine whether the electrolyte in question obeys the mass law. By substituting $1/λ$ for α, the mass law, $α^2 c / 1 - α = K$, can be transformed into the equation $1/λ = 1/λ_0 + (1/Kλ_0^2)cλ$, which is a linear relation between $1/λ$ and $cλ$ We have preferred, merely for convenience, to plot the value 100/λ against the specific conductivity ($= λc/1000$) This can, of course not affect the conclusions

In Fig. 3 are found a number of such plots drawn to the data found in Table I. The curve labeled AA corresponds to the data in Columns 4 and 6 of the table; namely, to the conductivities obtained by subtracting the conductivity of the pure solvent from the observed conductivity of

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[1] Calculated from the conductivities from which the conductivity of the solvent has been subtracted.

[2] The measurements for number 2 were made while the bath was 0.05° too low.

[3] THIS JOURNAL, **35**, 1324 (1913) See also Noyes, *Carnegie Publications*, **63**.

the solutions.[1]   It will be seen that for concentrations lying between 0.0438 and 0.3 the data conform very well to a straight line.[2]   The plot on which these curves were originally made was drawn to such a scale that deviations
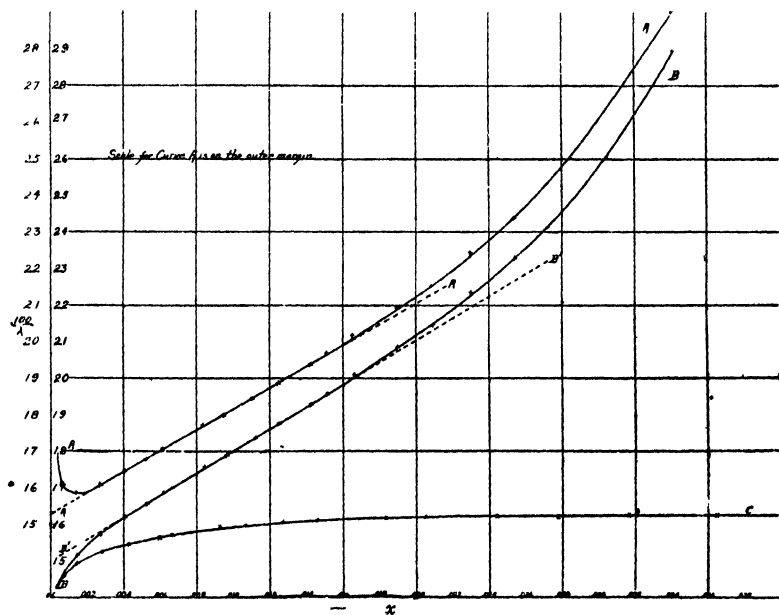
Fig. 3.

from the straight line corresponding to 0.1% could readily be observed and none of the values departed from the straight line by more than 0.2%, which is within the experimental error when one is dealing with a solvent so sensitive to moisture as is formic acid.

It is further to be noted that the conductivities corresponding to concentrations above and below these limits depart from the straight line. The higher concentrations are to be discussed below.   It is self-evident from the character of the plot that the deviations in the low concentrations mean that the observed conductivities are smaller than is required for conformity to the mass law.   Now it will be recalled that the conductivities used in plotting Curve *AA* were the values obtained by subtracting the conductivity of the pure solvent from the observed conductivity of the solutions.   But the solutions contain highly ionized sodium formate and the effect of the presence of the formate ion would be to repress the

[1] The scale of ordinates for this curve is found on the outer left-hand margin of the plot.

[2] The dotted line *A'A'* is this straight line extended.

ionization of the formic acid, and, therefore, to diminish its conductivity. Hence, the conductivity obtained by subtracting the total conductivity of the acid should be too small, and the values of $100/\lambda$ too large, which would account for the upward trend of the curve in the dilute solutions. Of course, the same thing would be true for the more concentrated solutions, but in these the conductivity of the solution is so large that the role played by the conductivity of the solvent is of less importance. This point will receive further elaboration in the next paragraph. By neglecting the upward turn of this curve and extending the straight line portion to the axis of ordinate, a value for the equivalent conductivity at infinite dilution may be obtained.[1]   This is found to be 65.4, and from it, or from 100 over this value, the degree of ionization, α_a, for the concentrations in the range just discussed and the ionization constant, K_a, can be calculated.[2]   These values are found in Columns 8 and 10 of the table.

In view of the probability that the presence of formate ion in the solutions represses the ionization of the solvent and, therefore, decreases its conductivity, a second curve, BB in Fig. 3,[3] has been plotted, using the conductivities uncorrected for the conductivity of the solvent.[4]   The lower concentrations again deviate from the straight line, this time, however, in the opposite direction. This deviation indicates that the conductivities employed for these concentrations in making this curve are too large. Two possible explanations can be offered for this phenomenon. In the first place, it is possible that in the more dilute solutions the concentration of formate ion, resulting from the ionization of sodium formate, is sufficient to repress the ionization of the acid partially, but not sufficiently great to repress it completely. The other possible explanation is that the observed conductivity of the solvent is not entirely due to its ionization, but is in part due to impurities present even in our best acid. A preliminary calculation which we have made shows that really both causes are operative in producing the deviation noted, but that the presence of an impurity, whose conductivity is not affected by the ions of sodium formate, seems to be the most important factor.[5]   This impurity is

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[1] On the assumption that the mass law really holds to infinite dilution. It is shown below that the deviations in the dilute solutions do not indicate deviation from the law, as they are due solely to the high conductivity of the solvent.

[2] Owing to the fact that the values of λ occur several times in the equilibrium law equation, the deviations of the constants from the mean (about $1\%+$) are greater than the deviations of the conductivities from the straight line. There is no deviation in the constants which cannot be accounted for by an experimental error of less than 0.2%.

[3] A portion of this curve is repeated in Fig. 4, labeled "Na," This enables a comparison with the other curves there given.

[4] The scale of ordinates for Curve BB in Fig 3 is found on the inner left-hand margin of the plot.

[5] The calculation was made as follows: We assumed that the conductivity of the

probably water into which the formic acid seems to be continuously decomposing   This conclusion receives strong support in the fact that the deviation under discussion is not observed in the solutions of hydrogen chloride, which contain hydrogen ion capable of repressing the ionization of both the formic acid and of the water   Since, therefore, the conductivity of the solvent is due chiefly to an impurity unaffected by the presence of the salt, the decrease in the conductivity due to the latter can only be very small, and we should expect that the data corrected for the conductivity of the solvent should more closely represent the true conductivity of the solute   An inspection of the curves shows that the one for the corrected conductivities deviates less from the straight line in the dilute solutions than does the other [1]   Nevertheless we have calculated the degrees of ionization and the ionization constants from the data uncorrected for the conductivity of the solvent and have presented them in Columns 7 and 9 of the table   It will be seen that they do not differ very much from the others   On this account we have occasionally used these data in the discussions, as they are a little simpler to handle, but whenever it is important to use absolute values for these data, the conductivities corrected for the conductivity of the solvent should be used

It appears, therefore, that sodium formate, when dissolved and ionized in (anhydrous) formic acid, obeys the law of mass action up to a concentration of about 0 3 molar when the degree of ionization is calculated directly from the conductivity of the solutions   Above this concentration the degree of ionization calculated in this way is less than it should be for continued agreement with the law, and as the concentration increases the deviation gradually becomes greater   This is the reverse of the kind of deviation observed in dilute aqueous solutions of strong electrolytes   It is, however, the kind of deviation which is to be expected according to the kinetic theory, for in the higher concentrations the volume actually occupied by the dissolved substance must become appreciably large in comparison with the total volume of the solution [2]   Should this be the correct interpretation of the deviation which we have observed in the concentrated solutions, it should be possible to make a correction for the volume

solvent (6×10^{-5}) is entirely due to its ionization and calculated from this the ion product constant of the solvent, using for the equivalent conductivity at infinite dilution the value 75 which we have obtained for hydrochloric acid   (A calculation made using 220 led to the same results)   From the ion product constant thus found, we calculated the degree of ionization of the solvent in the presence of the amount of sodium formate contained in the dilute solutions and from this the conductivity of the solvent in these solutions   The maximum value thus found was only 8×10^{-6}, which, while not entirely negligible, is not sufficient to account for the whole deviation

[1] In examining the curves of Fig 3 it must be borne in mind that the axis of abscissae is different for the two curves under discussion   If drawn to the same origin of axes the two curves would be very close together

[2] See Ostwald Z physik Chem, **2**, 270 (1888)

b, of dissolved substance by writing the equilibrium law in the form of the equation

$$\frac{\alpha^2}{(1 - \alpha)(v - b)} = K' \tag{1}$$

in which v is the volume of the solution. The volume b is the sum of the volume of the undissociated molecules plus that of the ions and, unless we make some assumptions in regard to the relative values of these volumes, the equation cannot be solved. The simplest assumptions to make in order to test the equation are: (1) that the sum of v_p, the volume of one gram ion of the positive ion, plus v_n, the volume of the corresponding quantity of the negative ion, is very large compared to v_m, the volume of one gram molecule of undissociated salt; (2) that v_p plus v_n is twice as large as v_m; (3) that v_p plus v_n is equal to v_m and, (4) that v_p plus v_n is negligibly small compared to v_m. Calculation shows that the first two assumptions lead to values for K' which are not even approximately constant. In Table II are given the equilibrium constants K_a without correction taken

TABLE II.

No.[1]	ϵ.	K_a.[2]	K'_3.[2]	K'_4[2]
2[s]	0.04381	0.816	0.816	0.816
8	0.06670	0.817	0.818	0.817
1[s]	0.08763	0.814	0.816	0.814
1	0.1046	0.811	0.814	0.812
7	0.1484	0.812	0.817	0 814
9	0.1718	0.827	0.834	0.829
4	0 2043	0 815	0.825	0 819
6	0.2351	0.816	0.829	0 821
3[e]	0.2760	0.816	0.834	0.823
13	0.2974	0.805	0.825	0.815
11	0.3338	0.795	0.820	0.808
14	0.3968	0 788	0.824	0 809
15	0 5157	0.753	0.812	0 793
12	0.5933	0.737	0.816	0.796
16	0.9867	0.596	0.814	0.820
17	1.017	0 584	0.817	0.830

Mean, o 821   0.815

directly from Table I, the constants, K'_3, for the whole range of concentrations all recalculated on the basis of the third assumption and the corresponding constants K'_4, calculated on the basis of the fourth assumption. The equation resulting from the assumption that v_p plus v_n is equal to v_m is

[1] Number 2 has been omitted since the measurements were made at a somewhat lower temperature than was used for the others. Number 17 is from measurements made by Mr. Coleman who is continuing the work herein reported.

[2] The constants are calculated from the conductivities which have been corrected for the conductivity of the solvent.

$$\frac{\alpha^2 c}{(1 - \alpha)(1 - c^2 v_m)} = K'_3 \qquad (2)$$

and the values found for K'_3, in the table, are calculated by means of this equation, using the value 0.275 for v_m. The assumption that the volume of the ions is negligible leads to the equation

$$\frac{\alpha^2 c}{(1 - \alpha)(1 - c^2 v_m(1 - \alpha))} = K'_4 \qquad (3)$$

which was used in obtaining the values for K'_4, the value of v_m for this calculation being 0.6. All of the other data required for the calculations were taken from Table I. The calculations were made for the dilute solutions in which the uncorrected mass law holds as well as for the concentrated ones, in order to make sure that the volume correction introduces no discontinuities.

It will be noted that, up to the concentration 0.3, the original uncorrected values for the equilibrium constant are a little better than either of the corrected constants but that in the higher concentrations, for which the uncorrected mass law gives very rapidly falling values for K_a, both of the corrected equations yield fairly good constants. The maximum deviation of the values of K'_4 from the mean is 2.7%, which corresponds to an error in the measurement of the conductivities of about 0.6%, while the maximum deviation of K'_3 from the mean is 1.6% corresponding to an error of measurement of only 0.3%. In spite of this apparently fairly good agreement between the data and the demands of the equations, too much stress must not be laid upon these calculations. In the first place, while the mean deviations, especially in the case of K'_3, are not much larger than might be expected from the probable errors of measurement, they are not as irregular as might be expected from deviations which are due entirely to experimental error. In the second place, the values of the term v_m are larger than one would expect. Thus, if we accept the results as meaning that the deviations observed in the concentrated solutions are completely explicable on the basis of the volume occupied by the solute, we must conclude that in a molar solution the dissolved substance occupies about 0.3 of the total volume. This, of course, would not be probable unless the molecules are extensively solvated. Finally, in making deductions from these equations, the fact that the volume correction introduces a third constant, v_m, into the equations must not be overlooked, because an equation with three constants in general fits a given set of data better than does a two constant equation. Consequently, we can now go no farther than to say that very likely the deviations in concentrated solutions are at least partially[1] due to the volume occupied by the solute, that this volume is probably quite large and that the volume of

[1] It is not unlikely that the effect of the viscosity will have to be taken into consideration in the more concentrated solutions. See p. 1606.

the ions is probably considerably less than that of the undissociated mole-cules. It is hoped that further work, to be carried out on more concentrated solutions of the formates, will definitely settle these points.

Thus far the conductivities have been discussed without reference to the viscosities of the solutions. It seems quite impossible that the agreement found for the conductivity, uncorrected for the viscosity, of sodium formate solutions in formic acid with the mass law can be accidental in character. Furthermore, we have found, as is to be shown, that what is true of sodium formate is true likewise of potassium formate, of ammonium formate, of phenyl ammonium formate and of hydrogen chloride in the same solvent and no accident could be responsible for this array of evidence. Hence, we believed that these solutions might be particularly favorable for deciding on the nature of the effect produced by viscosity changes and some preliminary measurements were therefore made. The viscosities were measured in a small Ostwald viscometer of such dimensions that the pure acid flowed out in about 100 seconds. From the type of instrument employed, results of the highest degree of reliability cannot be expected, but the results are sufficiently accurate to give a preliminary survey of the field. At the same time, it was necessary to determine the densities of the solutions. This was done in a special 25 cc. flask with narrow graduated neck and gave measurements accurate to about 0.1% or better, which is fully adequate for our purpose. The results of these measurements are tabulated in Table III. Column 1 gives the concentration; Column 2 the density d; Column 3 the viscosity η, and Column 4, a constant, A, calculated from the viscosities on the basis that the variation of these with the concentration is a linear function. The experimental values for the densities can be very accurately reproduced by the equation:

$$d = 1.2142 + 0.0356c.$$

TABLE III —THE RELATIVE VISCOSITIES AND DENSITIES OF SODIUM FORMATE SOLUTIONS IN FORMIC ACID AT 25°.

c.	d	η[1]	A.
0 0000	1 2142	0.0162	...
0.04228	1 2156	0 01669	0 01182
0 06941	1 2162	0 01700	0 01153
0 1124	1 2183	0 01743	0 01094
0 2382	1 2228	0 01892	0 01142
0 4460	1 2298	0 02139	0 01164
0 5759	1 2342	0 02302	0 01182
0 7435	1 2400	0 02532	0 01227
0 9876	1 2497	0 02926	0 01325

[1] These viscosities are only relative values. No effort was made to determine the absolute value for the pure acid, and as the data found in the literature differed considerably from each other, the rounded figure 0.0162 was chosen for the pure acid. Since we have no means of determining the accuracy of the viscosity data until they have been, at least in part, repeated with a more reliable instrument, we have given the number of decimal places which correspond to the "reproducibility" of the results.

It will be observed that the values of A show a decided minimum. The deviation from a straight line is not very great, amounting to a few per cent. In calculating the viscosities corresponding to the concentrations required for the conductivities, a value for the constant A was chosen from the table by interpolation and the viscosity calculated by a straight line formula of the form.

$$\eta = 0.0162 + Ac. \tag{2}$$

By choosing for each concentration suitable values for A the experimentally determined viscosities can thus be very well reproduced. Table IV gives the results of the viscosity calculations. Column 1 again gives the number of the conductivity determination, Column 2 the concentration; Column 3, the value for A for the respective concentrations calculated as described above; Column 4 the viscosities calculated according to equation 2; Column 5, the value of a hypothetical, corrected conductivity calculated on the basis of the equation

$$\chi_\eta = \chi \cdot \eta/\eta_0$$

in which η is the viscosity of the solution, η_0 the viscosity of the pure solvent, χ the specific conductivity of the solution not corrected for the conductivity of the solvent, and χ_η the hypothetical, corrected specific conductivity. Column 6 gives the value of $100/\lambda_\eta$ as calculated from the "corrected specific conductivity" of Column 5 and the concentration.

TABLE IV —CONDUCTIVITIES OF NaOCHO AT 25° CORRECTED FOR VISCOSITY.

No	c	A	η[1]	χ_η	$100/\lambda_\eta$
0	0		0 01620	..	...
5s	0 005477	0 012	0 01627	0 0003852	1 427
4s	0 01095	0 012	0 01633	0 0007517	1 457
3s	0 02190	0 012	0 01646	0 0014685	1 492
2s	0 04381	0 0118	0 01672	0 002878	1 522
8	0 06670	0 0113	0 01697	0 004310	1 548
1s	0 08763	0 0112	0 1718	0 005598	1 565
1	0 1046	0 0110	0 01735	0 0066375	1 576
7	0 1484	0 0111	0 01785	0 009298	1 596
9	0 1718	0 0112	∩ 01812	0 010745	1 599
4	0 2043	0 0113	0 01851	0 01270	1 608
6	0.2351	0 0114	0 01888	0 01459	1 611
13	0 2974	0 01145	0 01960	0 018355	1 620
11	0 3338	0 0115	0 02004	0 02055	1 624
14	0 3968	0 0116	0 02080	0 02442	1 625
2[4]	0 4500	0 01165	0 02144	0 02774	1 622
15	0 5157	0 01174	0.02225	0 03166	1 628
12	0 5933	0 01187	0 02324	0 03652	1 625
16	0 9876	[2]	0 02928	0 06217[3]	1 589

[1] See footnote 1, Table III.

[2] This concentration is one for which the viscosity was directly determined.

[3] There was no room for this value on the plot

[4] The measurement of the conductivity was made while the bath was 0.05° too low.

The values of $100/\lambda_v$, taken from Table IV, have been plotted against the specific conductivities "corrected for viscosity" taken from the same table. The curve is labeled CC^1 on Fig. 3. The portion of the curve corresponding to concentrations up to 0.3 molar is not a straight line.[2] Above this concentration the curve is almost a straight line. Up to about 0.6 molar the maximum deviation from the straight line is only about 0.5% and even at the most concentrated solution measured, 0.9876 molar, the deviation may be due to error in the viscosity measurements, as it is well known that the small viscometers of the type used may deviate quite a little from Poiseuille's law when the relative viscosities measured differ as much as they do in the case of these solutions.[3] We may, therefore, treat the curve, for the present, as if it were a straight line, parallel to the axis of specific conductivities. Such a line does not, however, indicate agreement with the demands of the equilibrium law. For the curve means, if the conductivities corrected for viscosity are to be used in calculating the degree of ionization, that, as we go from dilute to concentrated solutions, the degree of ionization first decreases and then becomes constant and remains constant to very high concentrations.[4] Such a conclusion is not even qualitatively in agreement with our ideas of chemical equilibrium.[5] Consequently, it seems very doubtful to us

[1] The scale of ordinates for this curve is found on the inside of the left-hand margin of the plot.

[2] This cannot be due to the effect of the conductivity of the solvent. In the first place, the corresponding curves for the data which have not been "corrected" for viscosity are straight lines at much lower concentrations. In the second place, it can be shown that the influence of the conductivity of the solvent upon the character of the curve ceases above 0.05 molar. The data given in Table IV have not been corrected for the conductivity of the solvent. If this correction is made and the resulting data are plotted and compared with curve CC, it will be found that the two curves are entirely similar until we get considerably below the concentration 0.05 molar, where the doubly corrected curve flattens out and gradually turns upward. From this it is clear that it is only below 0.05 molar that the conductivity of the solvent affects the character of the curve.

[3] On the other hand, it is possible that these deviations from the straight line are real and that there is a true maximum at about 0.5 molar. The deviation can be only very slight, however. The data for potassium formate show a similar, but even less-pronounced maximum (deviation from the straight line only 0.2%), while in the case of ammonium formate there is a more clearly defined maximum. It will require more accurate data, which are now being obtained, to decide the question. The conclusions which we have tentatively reached in the main body of this paper would not be affected if the curves show a maximum instead of being horizontal straight lines.

[4] If we consider the curve to have a real maximum, we must conclude that the degree of ionization has a minimum at about 0.5 molar.

[5] Robertson and Acree, *Am. Chem. J.*, 49, 502 (1913) have found that when they applied the viscosity correction to some of their conductivity data somewhat similar results were obtained.

that the application of the viscosity correction[1] is justified in these solutions.

Since there is, however, a great deal of evidence that the viscosity has, in many solutions, a decided effect upon the mobilities of the ions, there must be a reason why, in the case of the solutions of the formates in formic acid which we have investigated, the viscosity should have no such influence. There are a number of conceivable explanations. In the first place, it is possible that in the dilute solutions the ions are extensively solvated and that as the concentration increases they lose their formic acid of solvation and thus become smaller.[2] Such a progressive change in the volume of the ions could, of course, counteract the increase in viscosity. It does not seem, however, as if this could be the correct interpretation, as the decrease in volume necessary to produce the required result is greater than we have reason to believe likely to occur.[3]

A much more reasonable explanation for the absence of a noticeable viscosity effect is the following: Kraus[4] has suggested that in many organic solvents the great increase in viscosity with increasing concentration is due to the presence in the solutions of a relatively small number of very large undissociated molecules and that these, while they greatly decrease the fluidity of the solution as measured by the rate of flow through a capillary tube, do not greatly affect the mobility of the ions. This explanation is not in contradiction to any of the commonly cited theories concerning the flow of particles through viscous media, since these theories are based on the assumption that the molecules of the diffusing substance are large compared to the molecules of the viscous medium. Furthermore, the direct experimental evidence of these theories has been obtained under conditions in which these assumptions are justified. We have some evidence that, in the solutions now under discussion, the reverse of these assumptions is true. In the first place, the increase of the viscosity as the concentration increases is very large, indicating that the molecules which produce the viscosity change are very large. In the second place, although the evidence is indirect and not yet definitely established, the behavior of the concentrated solutions[5] seems to indicate that the ions

[1] A number of modifications of the simple viscosity correction have been suggested by Green, Johnston, Washburn, Kraus and others For references, see the articles by Kraus cited below. We have, so far as the data permit, applied such modified viscosity corrections, but have found that no essential changes have resulted. These calculations are therefore not given.

[2] The same suggestion has been made for aqueous solutions. See for example, Hartley, Thomas and Applebey, *J. Chem. Soc.*, **93**, 555 (1908); Green, *Ibid.*, **93**, 2033; Bousfield, *Z. physik. Chem.*, **53**, 257 (1903); Washburn, *Trans Am. Electrochem. Soc.*, **21**, 128 (1912).

[3] See Kraus, THIS JOURNAL, **36**, 35 (1914).

[4] *Loc. cit.* See also Washburn, *loc. cit.*, p. 30, *et seq.*

[5] See page 1602.

are considerably smaller than the undissociated molecules. These are exactly the conditions which, according to Kraus, tend to make relatively small the effect of viscosity increase upon the conductivity of solutions.

In view, therefore, of the possibility of explaining the apparent absence of viscosity influence and especially because of the excellent agreement between the data for uncorrected conductivities and the demands of the law of chemical equilibrium, we believe that the usual viscosity correction should be not applied in these solutions.[1]   As has been already mentioned this conclusion receives added confirmation from the fact that thus far in all of the solutions investigated by us in this solvent the same conditions are found.[2]

Potassium Formate.

The potassium formate was prepared by treating pure potassium carbonate with a large excess of boiling formic acid, which had been purified by the method described. The resulting salt was recrystallized several times from the pure acid. When apparently dry, the salt was found still to contain as much as 20% of the acid. This was removed by heating the substance to about 150° (which is a little below the melting point of the pure salt) for several days until it reached constant weight. The resulting solid analyzed to 99.6% potassium formate. The residual acid, which it probably contained, could doubtlessly have been driven out by melting the salt, but as the presence of acid could not affect the results, it was thought better to leave the salt in the condition described rather than to risk the danger of decomposition by further heating.

The solutions were made up as was described for sodium formate. The potassium salt is, however, far more hygroscopic than the sodium salt and consequently there is much greater liability of slight deviations. In spite of this, the data for this salt are as concordant as they are for the sodium formate. The data for the conductivity measurements will be found in Table V, the arrangement of this table being the same as for Table I.

It will be seen from the table that the conductivity data agree very well with the mass law whether they be "corrected" for the conductivity of the solvent or not. As in the case of sodium formate, deviation from the straight line, which represents the behavior in case agreement with the

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[1] It is not unlikely that in the concentrated solutions the viscosity effect becomes noticeable.

[2] Solutions of other uni-univalent formates are being investigated in the hope that in some of them the viscosity conditions will not be like those thus far met with. This may lead to a definite means of proving our conclusions. Furthermore, conductivity determinations of mixed solutions will be made in order to see whether the conductivities thus found will agree with the mass law and the degrees of ionization as calculated in this paper. Finally, transference experiments are planned to complete the data necessary for a complete elucidation of the points discussed.

TABLE V.—CONDUCTIVITY OF KOCHO AT 25°.

No.[1]	c	x	xₐ	100/λ	100/λₐ	α.	αₐ	K.	Kₐ.
0	0	.	...	1 430	1.452				
5s	0 01056	0 000759	0 000696	1 391	1 514				
4s	0 02112	0 001482	0 001419	1 425	1 488				
14	0 4052	0 002756	0 002693	1 470	1 505				
3s	0 4224	0 002864	0 002801	1 475	1 508				
3	0 5480	0 003667	0 003603	1 495	1 521				
13	0 06342	0 004210	0 004147	1 506	1 529	[0 95]		[1 11]	
9	0 07661	0 005000	0 004974	1 533	1 552	[0 93]	[0 935]	[0 992]	[1 036]
2s	0 08448	0 005474	0 005411	1 543	1 561	[0 927]	[0 930]	[0 991]	[1 05]
10	0 09464	0 006065	0 006002	1 560	1 577	0 917	0 921	0 955	1 006
8	0 1059	0 006901	0 006638	1 581	1 596	0 904	0 910	0 907	0 9761
15	0 1137	0 007171	0 007108	1 585	1 599	0 902	0 909	0 946	1 027
4	0 1270	0 007917	0 007854	1 604	1 617	0 891	0 898	0 930	1 004
16	0 1712	0 01036	0 01030	1 652	1 662	0 866	0 874	0 954	1 035
5	0 2121	0 01249	0 01243	1 698	1 706	0 842	0 851	0 953	1 008
11	0 2627	0 01499	0 01493	1 751	1 759	0 817	0 825	0 956	1 026
12	0 3043	0 01696	0 01690	1 793	1 800	0 797	0 807	0 955	1 024
6	0 3195	0 01765	0 01759	1 810	1 816	0 790	0 800	0 950	1 019
19	0 3917	0 02086	0 02080	1 877	1 883	0 762	0 771	0 954	1 017
17	0 4432	0 02301	0 02295	1 922	1 927	0 744	0 753	0 948	1 021
18	0 6104	0 02918	0 02912	2 094	2 098	0 683	0 692	[0 898]	[0 950]

law exists, is found above and below certain limits, the range of agreement in this case being from 0.09 to above 0.45 molar. Since the nature of the deviation in the low concentrations is of exactly the same kind as in the case of the sodium salt, we may again assume that it is due to a small residual conductivity of the acid, a residual conductivity caused chiefly by some impurity whose degree of ionization is not repressed by the ions of the potassium formate.

The concentrated solutions also are entirely analogous, the deviation from the law of mass action of both being in the sense that the degree of ionization is *too small*. In the case of the potassium salt the deviation begins at a higher concentration than in the case of the sodium salt. On account of the similarity of the two cases, only one curve is shown for potassium formate, namely, the one for the conductivities "uncorrected" for the conductivity of the solvent. It is found in Fig. 4 and is labeled K.

The viscosities and densities were determined in the manner described for the sodium salt. The viscosities corresponding to the concentrations were calculated from the values found in Table VI just as has been described for the other solutions and a set of conductivities "corrected for viscosity" calculated as before. These, and the corresponding values of $100/\lambda_\eta$, are found in Table VII.

[1] Nos. 1 and 2 were made with a salt containing 20% acid and are, therefore, not included   Number 1s was practically identical with number 16 and is not included Numbers 8 and 4, do not lie well on the curve but they are practically duplicated in numbers 15 and 16 which agree very well

x
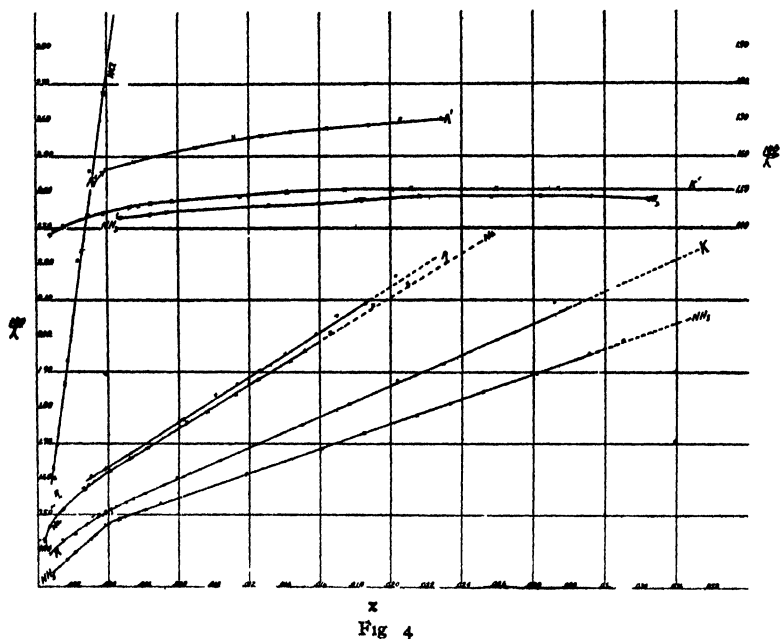
Fig 4

TABLE VI.—DENSITY AND RELATIVE VISCOSITY[1] OF KOCHO SOLUTIONS AT 25°.

c	d	A	η
o	1 2142		o 0162
o 0548	1 2166	o 0109	o 01680
o 0733		o 0108	0.01699
o 0176		o 0105	o 01743
o 1270	1 2201		
o 1787		o 01063	o 01810
o 1888		o 0106	o 01820
0.2099		o 0101	o 01832
o 2121	1 2230		
o 2619		o 01008	o 01884
o 2878	1 2266	o 0097	o 01899
o 3195	1 2282	o 01004	0,01941
o 3832	1 2324		
9/3917		o 01009	o 02015
o 4445		o 01005	o 02067
o 6104	1 2420	o 01030	0.02237

The density data of Table VI can be reproduced with an accuracy of better than 0.01% by the equation

$$d = 1.2142 + 0.045c.$$

[1] See footnote, Table III.

TABLE VII.—CONDUCTIVITY OF KOCHO SOLUTIONS "CORRECTED FOR VISCOSITY" AT 25°

No [1]	c	η [2]	x_η	$100/\lambda_\eta$.
0	0	0 0162		...
5s	0 01056	0 01632	0 000765	1 381
4s	0 02112	0 01643	0 001503	1 405
3s	0 04224	0 01664	0 002945	1 434
3	0 05480	0 01680	0.003803	1.441
13	0.06342	0 01690	0 004392	1 444
9	0 07661	0 01703	0 005256	1 458
2s	0 08448	0 01710	0 005778	1 462
10	0 09464	0 01721	0 006443	1 469
15	0 1137	0 01741	0 007707	1 474
16	0 1712	0 01801	0 01152	1 487
5	0 2121	0 01834	0 01414	1 500
11	0 2627	0 01885	0 01745	1 506
12	0 3043	0 01927	0 02008	1 508
6	0 3195	0 01943	0 02117	1 509
19	0 3917	0 02016	0 02596	1 509
17	0 4432	0 02068	0 02937	1 509
18	0 6104	0 02249	0 04051	1 507

The curve, K' (Fig. 4) for the conductivities "corrected for viscosity" is just like the corresponding one for sodium formate. It becomes parallel to the axis of specific conductivities at the concentration 0.26 molar and remains so to the highest concentration measured, 0.61 molar, which, however, is not nearly so high a concentration as the highest for sodium formate. It is not impossible that, at a corresponding concentration, the potassium formate curve might fall off from the straight line as does the other. The line as drawn deviates, in the parallel portion, only by 0.2% from the straight line.

Ammonium Formate.

Solutions of this salt have already been investigated by Schlesinger and Calvert.[3] It was deemed advisable to repeat this work for several reasons. In the first place, owing to the fact that their solutions were made by passing ammonia into the acid, only one or two analyses of the original solution could be made and the remaining solutions had to be made up by the dilution method. This is objectionable in the concentrated solutions, because of possible volume changes upon dilution which cannot readily be taken into account[4] as was pointed out in the earlier paper.

[1] Those experiments which on the curve for conductivities uncorrected for viscosity, appeared not to be in concordance with the others have been omitted in this table. There are practically duplicates for all such points Also points lying very close to one another have been represented here by only one of the two.

[2] See footnote 1, Table III.

[3] Loc. cit.

[4] In the more dilute solutions such changes cannot be of importance.

In the second place, the analyses were difficult to make because of the large excess of very volatile acid present in the solutions. In order to avoid these difficulties,[1] we prepared ammonium formate by saturating the purest acid with ammonia and recrystallizing the salt from formic acid solution. The salt thus prepared, was kept for weeks in a desiccator over potassium hydroxide. The final product was analyzed by distilling off the ammonia in the presence of sodium hydroxide. All of the usual precautions to prevent spattering of the alkali and of removing all of the ammonia by a current of pure air, etc, were observed. The acid in which the ammonia was collected was carefully standardized The salt used showed 100% ammonium formate within the limits of analytical error. From this salt the solutions were made up as in the case of the previously described salts.

The results of the measurements are given in Table VIII and in the curve labeled NH₃ in Fig. 4. This is the curve for the actually observed conductivities, those corrected for the conductivity of the solvent not being plotted because of their similarity to the sodium formate curve. The arrangement of Table VIII is identical with that of Table I

TABLE VIII.—CONDUCTIVITY OF NH₄OCHO AT 25°.

No[a]	c	x	x_d	$100/\lambda$	$100/\lambda_d$	α	α_d	K	K_d
0	0			1 410	1 430			.	..
4s	0.01162	0 000866	0 000803	1 340	1 447			.	
3s'[b]	0 02197	0 001598	0 001535	1 375	1 431				
14	0 02962	0 002125	0 002062	1 395	1 438				
2s'	0 04394	0 003065	0 003002	0 434	1 464				
2s	0 04646	0 003220	0 003157	1 443	1 472				.
13	0 06821	0 004581	0 004515	1 489	1 511	0 947	0 946	1 15	1 14
1s	0 09293	0 006134	0 006071	1 515	1 531	0 931	0 934	1 16	1 23
2	0 1070	0 006988	0 006923	1 532	1 546	0 920	0 925	1 14	1 22
6	0 1914	0 01184	0 01177	1 617	1 636	0 872	0 879	1 14	1 23
1	0 2711	0 01609	0 01603	1 685	1 691	0 837	0 845	1 16	1 23
12	0 3207	0 01855	0 01848	1 728	1 735	0 816	0 824	1 16	1 24
10	0 3220	0 01858	0 01852	1 732	1 739	0 814	0 822	1 15	1 23
5	0 3822	0 02154	0 02147	1 775	1 780	0 794	0.803	[1 17][d]	[1 25][d]
11	0 4236	0 02336	0 02329	1 813	1 819	0 778	0 786	1 15	1 23
4	0 4643	0 02519	0 02512	1 843	1 848	0 765	0 774	1.16	1 23
3	0 5351	0 02825	0 02819	1 894	1 898	0 744	0 753	1 16	1.23
8	0 6081	0 03115	0 03108	1 952	1 956	0 723	0 731	1.15	1 21
7	0 6575	0.03304	0.03298	1 990	1 994	0 709	0 717	[1 13]	[1 20]

[1] Our procedure is not as reliable for the dilute solutions as will be shown below.

[a] Two series were made in this case because the data did not agree with those of Calvert and the curve was not just like the sodium formate curve in the dilute solutions The corresponding data have been numbered s and s', respectively. They are seen to be concordant.

[b] Made up in a calibrated 50 cc. flask.

[d] This point is apparently incorrect. This can be seen by reference to the plot.

It is evident that the results for ammonium formate are, in general, like those for sodium and potassium formate and that they fully confirm the results of Schlesinger and Calvert.[1] The deviation in the more concentrated solutions begins above 0.55 molar.[2] A slight difference between the ammonium salt and the others is found in the dilute solutions, which fall away from the straight line much more rapidly than do the corresponding points for the other salts. We ascribe this to impurity in the ammonium formate, because Schlesinger and Calvert's results were entirely analogous to ours on sodium and potassium formates and because we obtained a similar result with an ammonium formate sample which had been freshly prepared. This sample of salt was not then used because it still contained an excess of formic acid. The somewhat different result obtained after the salt has been kept for some time can be explained by assuming partial (very slight) transformation into formamide. This impurity would not affect the concentrated solutions because its conductivity is very small.[3] But in the more dilute solutions, where it would be more highly ionized, its effect would be to make the apparent conductivity of the ammonium formate too large. This explanation is offered only as a suggestion; further work would be required to settle the point. It is, however, a matter of little importance, since the agreement with data for the salts in the more concentrated solutions is excellent.

The viscosity and density data are given in Table IX.

TABLE IX —VISCOSITY AND DENSITY OF NH_4OCHO SOLUTIONS AT 25°

c	d	η [4]	A
0 8847	1 2273	0 02418	0 00903
0 8290	1 2269	0 02356	0 00888
0 5221	1 2222	0 02063	0 00848
0 3676	1.2203	0 01923	0 00824
0 3207		0 01888	0 00835
0 2868	1 2189	0 01859	0 00833
0 2495	1 2186	0 01841	0 00886
0 1422	1 2166	0 01745	0 00907
0 05978	1 2152	0 01680	0 01004
0	1 2142	0 0162^1	

In Table X are given the calculations for the "corrected conductivities," calculated as before.

[1] The line drawn from their data does not fall exactly on ours, probably because of the more accurate analysis permitted by our method of making up the solutions.

[2] The last one of our points to fall on the straight line is for the concentration 0.535. The next point 0 608, lies slightly above the line, but S and C found that the point for 0 55 was still on the line.

[3] The concentrated solutions of the fresh and the old salt showed good agreement.

[4] See footnote 1, Table III.

TABLE X.—CONDUCTIVITY OF NH$_4$OCHO "CORRECTED" FOR VISCOSITY AT 25°.

No.	c.[1]	A.	η.[3]	x_η	100/λ_η.
0	...	...	0.162	...	...
13	0.06821	0.01000	0.01688	0.004774	1.429
1	0.09293	0.00965	0.01710	0.006475	1.435
2	0.1070	0.00919	0.01718	0.007410	1 444
6	0.1914	0.00896	0.01791	0.01309	1.462
1	0.2711	0.00855	0.01852	0.01840	1.473
12	0.3207	...	0 01888	0.02162	1.483
10	0.3220	0.00833	0.01888	0.02165	1.487
5	0.3822	0.00826	0.01935	0 02573	[1.486][3]
11	0.4236	0.00834	0.01973	0.02845	1.489
4	0.4643	0.00838	0.02009	0.03124	1.486
3	0.5351	0.00850	0.02075	0.03618	1.479
8[4]	0.6081	0.00859	0.02143	0.04120	1.476
7[4]	0.6575	0.00866	0.02189	0.04464	1.473

The curve corresponding to the data in Table X is found in Fig. 4 and is labeled NH$_3$'. It is very similar to the corresponding curves for sodium and potassium formates. The portion corresponding to the concentrated solutions does not lie quite on a straight line parallel to the axis of specific conductivities, but shows a slight maximum. The deviation from a straight line is about 1%, but, since the maximum is quite regular, it may not be due to experimental error. If the data are correct, they would mean that the degree of ionization has a minimum at about 0.4 molar. A similar trend has been pointed out in the data for the other salts.

Phenyl Ammonium Formate.

The work was carried out exactly as for the other salts, except that aniline was used to make up the solutions instead of the salt itself. The accuracy of the work was somewhat interfered with by the fact that the solutions are not stable, probably because of anilide formation. By working rapidly, however, good results could be obtained, excepting that occasionally a reading was taken before temperature equilibrium was established. Usually, however, the change due to temperature adjustment could be distinguished from the other, slower change in the solutions. It took some experience before this was learned and for this reason the data found in the table are from the later experiments, as can be seen from the numbers. Because of this tendency of the solutions to undergo change, dilute solutions were not studied as a dilution series takes several hours at the best. In all other respects the experiments and the results

[1] The calculations for those concentrations at which the deviation due to the conductivity of the solvent are noticeable, have not been included in the table.

[3] See footnote, Table III.

[3] Concerning this point see footnote 3 on p. 1610.

[4] These points are not plotted on the curve as they lie beyond the field covered by the plot, but the curve is drawn so that it would include these points if it were extended.

are entirely analogous to the ones for the sodium and potassium salts. They require therefore, no further discussion. The data are found in Tables XI, XII and XIII, which correspond to analogous tables in the preceding and the curves are drawn in Fig. 4   The one labeled A is for the conductivity data without correction for the conductivity of the solvent and the one labeled A' is for the conductivity corrected for viscosity

TABLE XI —CONDUCTIVITY OF PHENYL AMMONIUM FORMATE AT 25°

No	c	x	x_a	$100/\lambda$	$100/\lambda_a$	α	α_a	K	K_a
0	0			1 514	1 545				
8	0 04866	0 003022	0 002960	1 610	1 644	0 940	0 940	0 719	0 714
28	0 06238	0 003828	0 003764	1 6295	1 657	0 929	0 932	0 742	0 802
29	0 08758	0 005231	0 005166	1 674	1 695	0 904	0 911	0 748	b 822
30	0 1466	0 008295	0 008231	1 768	1 782	0 856	0 867	0 748	0 829
22	0 1845	0 01006	0 009995	1 834	1 846	0 825	0 837	0 720	0 792
42	0 2105	0 01130	0 01124	1 863	1 874	0 813	0 824	0 742	0 815
21	0 2395	0 01260	0 01253	1 9015	1 911	0 796	0 808	0 745	0 817
26	0 2740	0 01404	0 01400	1 9515	1 960	0 776	0 788	0 736	0 804
20	0 3174	0 01582	0 01575	2 007	2 015	0 754	0 767	0 736	0 800
25	0 3494	0 01700	0 01694	2 055	2 063	0 737	0 749	0 721	0 780
31	0 3894	0 01865	0 01859	2 088	2 095	0 725	0 737	0 744	0 806
34	0 4391	0 02026	0 02026	2 167	2 174	0 699	0 711	[0 711]	[0 767]

TABLE XII —DENSITY AND VISCOSITY OF PHENYL AMMONIUM FORMATE SOLUTIONS AT 25°.

c	d	η [1]
1 0410	1 2133	0 02668
0 6276	1 2143	0 02231
0 4070	1 2148	0 02000
0 3316	1 2147	0 01943
0 1587	1 2146	0 01775
0 08122	1 2140	0 01704
0	1 2142	0 0162

TABLE XIII —CONDUCTIVITIES OF PHENYL AMMONIUM FORMATE AT 25°, "CORRECTED" FOR VISCOSITY

No	c	η [2]	x_η	$100/\lambda_\eta$
8	0 04866	0 01673	0 003121	1 559
28	0 06238	0 01689	0 003991	1 563
29	0 08758	0 01712	0 005528	1 584
30	0 1466	0 01764	0 009033	1 623
22	0 1845	0 01797	0 0116	1 653
24	0 2105	0 01832	0 01272	1 655
21	0 2395	0 01850	0 01438	1 665
26	0 2740	0 01890	0 01638	1 672
20	0 3174	0 01932	0 01886	1 683
25	0 3494	0 01958	0 02055	1 700
31	0 3894	0 01988	0 02289	1 702

[1] See footnote 1, Table III.
[2] See footnote to Table III

The latter is not a straight line, and shows no portion parallel to the axis of specific conductivity, probably because the work was not extended into sufficiently concentrated solutions. Deviation in the higher concentrations begins between 0.3 and 0.4 molar. The actual point of deviation is not definitely settled, because it is quite difficult to be sure that apparent deviation is not due to the changes occurring in the solutions, as was mentioned above. Judging from the curve, the most probable point is at about 0.3 molar.

Hydrogen Chloride.

Zanninovich-Tessarin[1] concluded from his measurements of the conductivity of solutions of hydrogen chloride in formic acid that there was practically no ionization, and from his measurements of the depression of the freezing point of formic acid by hydrogen chloride that the latter was associated in this solvent. As has already been pointed out by Schlesinger and Calvert,[2] if these conclusions are correct, salts such as ammonium chloride should be practically completely decomposed in formic acid solution into a formate and hydrogen chloride and the conductivity of the salt should, therefore, be practically the same as that of the corresponding formate. The work of Schlesinger and Calvert showed that the conductivity of ammonium chloride was entirely different from that of ammonium formate. For this reason, it seemed necessary to repeat the work of Zanninovich-Tessarin. On account of certain difficulties, which wo uld have required the construction of a new conductivity cell to obtain results of the degree of accuracy reached in the measurements on the formates, results accurate to only about one to 2% were sought. This degree of accuracy was sufficient to decide the question of the hydrolysis of salts, as well as to give a fairly definite idea of the behavior of hydrogen chloride in the solvent.

The measurements were made in cell No. 2, the solutions being made from one another by the dilution method. The original solution was prepared by passing carefully dried hydrogen chloride gas through formic acid contained in the conductivity cell. The undissolved gas was displaced by a current of dry air. Since the volume of the resulting solution was not the same as that of the original formic acid, both because of loss of acid by volatilization and because of the change in volume resulting from the dissolution of the gas, the concentrations could not be calculated in the ordinary way! Consequently, the portion of solution withdrawn from the cell in order to make the dilution was analyzed each time by precipitation of the chlorine as silver chloride. Two difficulties stood in the way of attaining great accuracy in the type of cell used for our other work. In the first place, the more concentrated solutions seem to lose hydrogen chlo-

[1] *Z. physik. Chem.*, **19**, 251 (1896).
[2] *Loc. cit.*

ide rapidly and the measurements are, therefore, made under great disadvantages. The more dilute solutions have a conductivity which is not
sufficiently greater than that of the pure solvent to give very trustworthy
results. Furthermore, the amount of silver chloride precipitated from
10 cc. of the dilute solutions is too little to allow of an analytical accuracy
of more than 1%, or less, without the use of the nephelometer However,
no attempt was made to refine the analytical method because of the other
difficulties mentioned. The results obtained, which are given in Table
XIV, show that the data of Zanninovich-Tessarin are incorrect and that

TABLE XIV —CONDUCTIVITY OF HCl IN FORMIC ACID AT 25°

No of series	c	λ	λ	α	K
0	0		80 0		
2	0 0080	0 000566	70 0	0 88	[0 0520]
3	0 0111	0 000768	69 2	0 86	[0 0449]
2	0 0150	0 000936	62 3	0 78	0 0415
1	0 0152	0 000931	61 4	0 77	0 0388
3	0 0195	0 00115	58 9	0 74	0 0407
2	0 0276	0 00148	53 7	0 67	0 0376
3	0 0328	0 00170	51 8	0.65	0 0392
2	0 0518	0 00234	45 2 •	0 57	0 0385
3	0 0570	0 00255	44 7	0 56	0 0404
2	0 0951	0 00355	37 4	0 47	0 0392
3	0 101	0 00377	37 4	0 47	0 0415
1	0 137	0 00454	33 1	0 41	0 0398
2	0 174	0 00528	30 0	0 38	0 0405
1	0 281	0 00732	26 0	0 32	[0 0438]
2	0 317	0 00801	25 3	0 32	[0 466]

formic acid solutions of hydrogen chloride are good conductors. The
reason for this divergence between our results and those of the former
investigator doubtless lies in the fact that the acid used by him as solvent
was very impure, as judged from its high initial conductivity. In the table
are given the results of three series of measurements made as described.
The first column gives the number of the series from which the data are
taken; the second the concentrations; the third the specific conductivity
uncorrected[1] for the conductivity of the solvent; the fourth, the equiva-

    [1] The uncorrected value is used, since the hydrogen ion would tend to
repress the ionization of the solvent. A curve drawn for the corrected conductivities was exactly of the same character as the one shown The extrapolated value of λ₀ from this curve is about 69   Two slight differences from
the data for the formates are to be noted In the first place, the correction for
the conductivity of the solvent has a greater effect on the constants and on the
value of λ₀ than it has in the case of the salts This is due to the much smaller conductivity of the hydrogen chloride solutions. In the second place, the deviation in
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The latter is not a straight line, and shows no portion parallel to the axis of specific conductivity, probably because the work was not extended into sufficiently concentrated solutions. Deviation in the higher concentrations begins between 0.3 and 0.4 molar. The actual point of deviation is not definitely settled, because it is quite difficult to be sure that apparent deviation is not due to the changes occurring in the solutions, as was mentioned above. Judging from the curve, the most probable point is at about 0.3 molar.

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The measurements were made in cell No. 2, the solutions being made from one another by the dilution method. The original solution was prepared by passing carefully dried hydrogen chloride gas through formic acid contained in the conductivity cell. The undissolved gas was displaced by a current of dry air. Since the volume of the resulting solution was not the same as that of the original formic acid, both because of loss of acid by volatilization and because of the change in volume resulting from the dissolution of the gas, the concentrations could not be calculated in the ordinary way.[*] Consequently, the portion of solution withdrawn from the cell in order to make the dilution was analyzed each time by precipitation of the chlorine as silver chloride. Two difficulties stood in the way of attaining great accuracy in the type of cell used for our other work. In the first place, the more concentrated solutions seem to lose hydrogen chlo-

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1	0 281	0 00732	26 0	0 32	[0 0438]
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formic acid solutions of hydrogen chloride are good conductors. The reason for this divergence between our results and those of the former investigator doubtless lies in the fact that the acid used by him as solvent was very impure, as judged from its high initial conductivity. In the table are given the results of three series of measurements made as described. The first column gives the number of the series from which the data are taken, the second the concentrations, the third the specific conductivity . uncorrected[1] for the conductivity of the solvent, the fourth, the equiva-

[1] The uncorrected value is used, since the hydrogen ion would tend to repress the ionization of the solvent A curve drawn for the corrected con ductivities was exactly of the same character as the one shown The extrapolated value of λ_0 from this curve is about 69 Two slight differences from the data for the formates are to be noted In the first place, the correction for the conductivity of the solvent has a greater effect on the constants and on the value of λ_0 than it has in the case of the salts This is due to the much smaller conductivity of the hydrogen chloride solutions. In the second place, the deviation in the dilute solutions observed in the case of the formates is not so noticeable here There are probably two reasons for this In the first place, the data are not so accurate for hydrogen chloride solutions and the plot is drawn to a smaller scale, so that small

lent conductivity in the usual units, and the fifth the degree of ionization, α. This latter value was obtained by plotting $100/\lambda$ against the specific conductivity and extending the straight line portion of the resulting curve to to the axis of ordinate as has already been described. This, of course, gives an extrapolated value for λ_0, namely, about 80. The plot obtained was practically a straight line between the concentrations 0.174–0.015. The points deviate from the line irregularly by the amount to be expected from the probable error of measurement—at most by 3%. Both above and below these concentrations the curve seems to depart from the straight line but it is very probable that this is due to experimental error—due in the concentrated solutions to loss of hydrogen chloride by volatilization in the course of the transfer of the solution from the cell to the water in which it was analyzed, and in the dilute solutions to the insufficient amount of silver chloride available for the analysis. The deviation in the dilute solutions begins at exceedingly low concentrations and is, in this respect, not like the deviation observed in the case of the formates
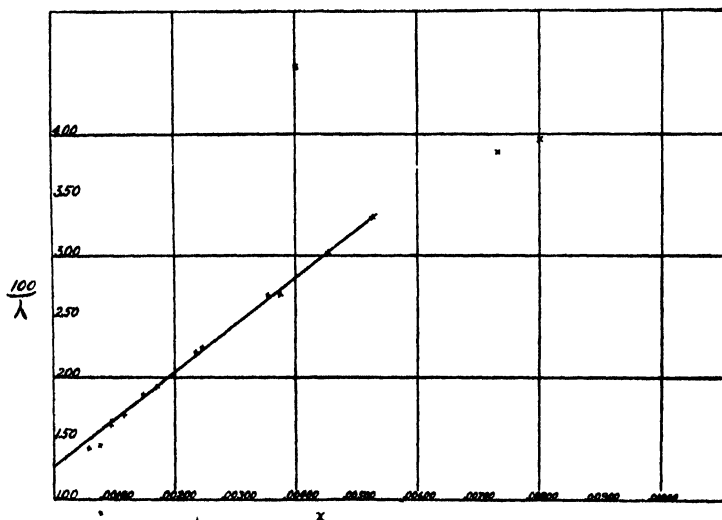
Fig. 5.

deviations are not so noticeable. In the second place, the hydrogen ion in these solutions must suppress not only the ionization of the formic acid but that of the water as well, which is probably present as impurity   (See p. 1599.) Hence there is no reason to suppose that the curves should show the type of deviation found in the case of the formates since this deviation was shown in part to be due to the conductivity of the water which is not affected by the ions of these salts.   Since it is probably repressed by the ions of the hydrogen chloride, we believe that here the data uncorrected for the conductivity of the solvent are the ones to use

as explained in footnote 1, page 1615. The curve is shown in Fig. 5 [1] The agreement of the curve with a straight line is again evidence that this solute, in formic acid solution, obeys the law of mass action The constants obtained according to this law are given in the last column of the table They were calculated directly from the conductivities and not from the data for α, which, as given in the table are rounded in the second decimal place It will be noted that the constants are fairly good, except for the high and low concentrations where the errors of measurement were large

It is interesting to note that in formic acid solutions hydrogen chloride is very much less dissociated than are the formates, the results for which are given in the preceding sections Thus the ionization constant for ammonium formate is 1 15 and for hydrogen chloride only 0 040 This is in agreement with Walden's assumption[2] that acidic substances are not as highly ionized in acid solvents as are basic substances It is also very interesting to note that the conductivity of hydrogen chloride in this solvent at infinite dilution seems to be only about 80, which is of the same order of magnitude as that of the formates investigated Hydrogen ion cannot, therefore, occupy the exceptional position in this solvent which it holds in aqueous solutions [3]

Since our results on the conductivities of these solutions differ so widely from those of Zanninovich Tessarin, it was natural to question his results on the freezing point depression As such measurements were considerably outside of the scope of this paper, only a few determinations were made They were carried out in an ordinary Beckmann freezing point apparatus, modified so as to allow the making of dilutions in it without exposing its contents to moisture, as well as to allow of the withdrawal of the solution in equilibrium with the solid solvent for analysis at the time the temperature reading was made As the Beckmann apparatus is liable to many errors the results will be stated only briefly Between the concentrations 0 026 and 0 36, the molecular lowering changed progressively from 42 to 29 While no great accuracy is claimed for these values, they at least show qualitative agreement with the results of the conductivity measurements and show that those of Zanninovich-Tessarin are incorrect here also Not only the nature of the change of the molecular freezing-point depression with change in concentration, but the value

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[1] In order to make comparison with the other curves possible, a part of this one is also shown in Fig 4 It is labeled "HCl"

[2] *Trans Far Soc* 6, 71 (1910)

[3] It is evident, therefore, that the exceptionally large migration velocity of hydrogen ion in aqueous solutions cannot be related essentially to the fact that hydrogen ion is a product of the ionization of water, since it is also a product of the dissociation of formic acid See also Kraus, *loc cit* and Hantzsch and Caldwell, *Z physik Chem*, **58**, 578 (1907)

27.7 obtained for the molecular freezing-point depression constant for this solvent by Raoult both indicate ionization and not association. Tessarin's value of about 13 must certainly be in error because of the impurity of his formic acid, which melted at 7.0° whereas the pure acid melts at about 8.4°.

Summary.

(1) The highly ionized solutions of sodium, phenyl ammonium, potassium and ammonium formates in (anhydrous) formic acid obey the law of mass action up to concentrations of from 0.3 to 0.6 molar, if the degree of ionization is calculated from the conductivities[1] to which no correction for the viscosity of the solutions is applied. The ionization constants of the salts in the order in which they are named have the values: 0.816, 0.814, 1.02 and 1.23. The same thing is true of solutions of hydrogen chloride, the ionization constant of which is only 0.04.[2] Above the concentrations mentioned, the formates show deviation from the mass law in the sense that the degree of ionization is less than it should be. This is the kind of deviation which is to be expected from the kinetic theory, if its cause lies in the reduction of the free space by the volume occupied by the solute itself. In this connection it is interesting to note that the data for sodium formate, up to the highest concentrations measured, show fair agreement with the equation

$$\frac{\alpha^2 c}{(1 - \alpha)(1 - v_m c^2)} = K$$

which is derived on the assumption that the deviation in the concentrated solutions is due to the cause suggested above. It is, however, not considered finally established that this agreement is reliable evidence of the correctness of the assumption.[3] There seems also to be a connection between the value of the highest concentration at which the law of chemical equilibrium holds and the value of the ionization constant. Thus ammonium formate, with a constant[4] of 1.23, begins to deviate above 0.55 molar; potassium formate, whose constant is 1.02, above 0.45 molar, and sodium and phenyl ammonium formates, whose constants are respectively, 0.816 and 0.814, both begin to deviate from the law at about 0.3 molar. It seems, therefore, that the greater the value of the ionization constant, the higher the point at which deviation begins. Of course, four cases is not a sufficiently large number to establish definitely a point

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[1] For a discussion of the conductivity of the pure solvent and its effect on the conductivity of the solutions see p. 1598.

[2] The limiting concentration for hydrogen chloride has not been determined.

[3] It was also assumed in deriving the equation that the volume of the ions is smaller than that of the undissociated molecules. For the complete discussion of this and other similar equations and of the data see p. 1599.

[4] These are the constants from the data uncorrected for the conductivity of the solvent.

of this sort. This regularity is pointed out, nevertheless, because, in view of the probable explanation offered above for the cause of this deviation, a regularity of this sort might prove of considerable theoretical interest. It is evident that it would lead to the conclusion that there is a relationship between the degree of ionization and the volume of the unionized molecule.[1]

(2) When the conductivities of the solutions are corrected in any of the usual ways for the viscosity of the solutions, and the degrees of ionization calculated from these corrected conductivities, the agreement with the mass law disappears. From the fact that the agreement of the uncorrected data in the more dilute solutions is so good and uniform in all of the cases investigated, and because there are possible explanations for the absence of viscosity effect, we conclude that the uncorrected conductivities are the ones to be used in these solutions for the calculation of the degree of ionization. This point has already been discussed in detail in the section in which the data for sodium formate are presented (p. 1604, et seq.). In this connection Table XV is of interest. It gives in Column 1 the name of the substance studied, in Column 2 the conductivity of its solution in water at infinite dilution, in Column 3 the observed conductivity at infinite dilution when formic acid is the solvent, and in Column 4 the conductivities of these same substances at infinite dilution in formic acid, calculated on the assumption that this conductivity is inversely proportional to the viscosities of the two solvents.

TABLE XV

Substance.	λ_0 in H_2O at 25°[2]	λ_0 in HCOOH at 25°[1]	λ_0 in HCOOH calc
NH_4OCHO	127.9	70 4	71 1
$KOCHO$..	128.4	69.4	71 3
$NaOCHO$..	104.9	66 0	58 5
$C_6H_5NH_3OCHO$.......	85.9	65 4	47 0
HCl......... ...	424.0	75 0	236.0

[1] This is pointed out merely as a possibility which must await further evidence for definite proof It is, however, in line with some of the more recent views on the nature of the process of dissociation See Perrin, *Les Atomes*, 1912, 228–231; Szyszkowski, *Compt. rend.*, 157, 761.

[2] Except for phenyl ammonium formate, these values are calculated from the migration velocities found in Landolt-Börnstein, Roth, *Physikalich-Chemische Tabellen*, 1912, 1124. The value for phenyl ammonium formate is obtained from Bredig's value for aniline hydrochloride (*Z. phys. Chem.*, 13, 216 (1899)), and is, of course, quite uncertain. The value for formate ion is also not exactly known, but would affect all results equally. The rounded values 0 009 and 0.0162 were used for the viscosities of water and formic acid, respectively.

[3] The λ_0 values here used are the averages of those obtained by neglecting the conductivity of the solvent and those obtained when the correction is made. As explained on p. 1615, footnote 1, the difference in the two λ_0 values is large only in the case of hydrogen chloride. In the other cases it is only about 1%.

It is quite clear that the calculated values do not agree at all with those found except in the case of potassium and ammonium formate. This fair agreement in two cases makes the disagreement in the others more striking. If none of the values showed agreement, the disagreement might be explained for the formates by the lack of an accurate value for the migration velocity for formate ion in aqueous solution and in the case of hydrogen chloride by the probable inaccuracy of our value for the formic acid solution (although the inaccuracy could not be nearly large enough to account for the enormous discrepancy in this particular case).[1] Or the disagreement might be explained by saying that the simple viscosity relationship assumed is not correct in any case. But since the relationship gives, in some cases, values which agree and in others values which disagree with the experimental ones, it is clearly shown that the difference in viscosity of the solvents does not affect all ions alike.[2] It is, therefore, not permissible to set up a general equation expressing a relationship between the conductivities at infinite dilution in various solvents and the viscosities alone.[3] In formic acid, for instance, the mobilities of the ions do not seem to differ from each other as much as they do in aqueous solutions.[4]

This work is being continued in this laboratory along the lines indicated in the body of the paper. In addition to the points already mentioned it may be stated that we are repeating some of the measurements at different temperatures from those at which the data herein reported were obtained, and that we are also studying formates of types higher than the uni-univalent ones.

THE HEAT OF VAPORIZATION OF NORMAL LIQUIDS.

BY JAMES KENDALL.

The theoretical study of the heat of vaporization of liquids– a branch of physical chemistry long neglected--has recently attracted a great deal of investigation. The subject is of interest from its connection with the equation of van der Waals and the problem of molecular attraction. A number of formulas for representing variation of heat of vaporization with temperature have lately been put forward; some of these claim a theoretical basis, some are admittedly empirical. During the past year,

[1] The data for HCl are discussed on p. 1616.

[2] This may be due to differences in the solvation of the various ions in the two solvents.

[3] See Walden, Z. physik. Chem , 55, 207 (1906) for references.

[4] See Kraus, loc cit.

in particular, the rate of appearance of new formulas has increased to the proportions of an epidemic.

It has seemed of importance, therefore, to the author, in view of previous work upon the subject, to make a critical examination of the various equations that have been proposed. Their relative theoretical merits - -a field already fruitful in polemics—are not touched upon at all in this paper. The sole point of investigation is agreement with the experimental data. In the present imperfect state of our knowledge of this subject, where even first principles are hotly disputed, it appears reasonable to apply to all equations the one practical test, free from any possible bias--the test of accuracy.

It is true that we possess no direct determinations of heats of vaporization for any normal liquid, throughout an extended temperature range, sufficiently trustworthy to be of value for the above purpose. However, the thermodynamical equation of Clausius and Clapeyron (see Equation 1 below) affords a method of obtaining the heat of vaporization indirectly by the measurement of other quantities. These quantities are all accurately determined for a large number of liquids and through a wide range of temperature in the extensive researches of Young and his collaborators.

The results of Young have recently been revised and published in collected form.[1] The necessary data are now available for thirty pure liquids, of which twenty-six are normal or non-associated.

It is impossible, from space considerations, to examine all of those in the present paper; consequently, a few typical cases have been selected. The agreement of the various formulas with the experimental results for octane, methyl, butyrate, carbon tetrachloride and fluorobenzene is tested in the tables given below

The above liquids were chosen, without previous knowledge as to the nature of the results they would supply, for the following reasons. It is important, in testing any function which varies with temperature, to be able to consider as large a temperature range as possible. Hence octane was selected from the ten hydrocarbons investigated by Young, since it possesses the highest critical temperature. (The lowest temperature for which data are available is o° in all cases.) Methyl butyrate was chosen as the typical example of the ten esters studied, for the same reason. The remaining liquids—carbon tetrachloride and fluorobenzene—are among those regarded by investigators as "characteristically" normal liquids;[2] both have, also, high critical temperatures. That the data selected are really representative may be confirmed by a study of the collected tables.[3]

[1] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).
[2] Applebey and Chapman, *J. Chem. Soc.*, **105**, 742 (1914).
[3] Mills, THIS JOURNAL, **31**, 1099 (1909)

The equations examined are developed briefly below: The following notation is employed.

T—absolute temperature
t—temperature centigrade
V—volume of one gram of saturated vapor.
d—density of liquid
D—density of saturated vapor
P_c—critical pressure
M—molecular weight

R—constant of gas equation, $PV = RT$, equal, under the units employed, to $62340/M$
T_c—critical temperature
v—volume of one gram of liquid
d_c—critical density
P—vapor pressure in mm. of mercury
L—total heat of vaporization[1] of one gram of liquid, expressed in calories

With this notation, the thermodynamical equation is expressed as follows:

$$L = 0.0431833 \ (dP/dT)T. \ (V — v) \tag{1}$$

(The numerical factor is the reciprocal of the value of the mechanical equivalent of heat under the units stated.) The heat of vaporization at any temperature is thus obtained in terms of T, V, v and dP/dT, and the degree of accuracy of the calculated value will depend upon the limits of experimental error in the determination of these quantities, and upon the relative effect of such errors in the calculation of the equation. These points have been carefully examined by Mills.[2] The conclusion drawn is that, except at zero centigrade and in the neighborhood of the critical temperature, the calculated values for the heat of vaporization are substantially true. At 0° C. the values derived are usually too high; near T_c the difficulty in the exact determination of dP/dT renders the results somewhat uncertain. The above equation may, therefore, be safely employed as a basis for comparison throughout the greater part of the experimental range, small divergences at 0° C. and near T_c being disregarded.

A simple formula developed by Mills:[3]

$$L = 0.0431833 \ P \ (V — v) + \mu'(\sqrt[3]{d} — \sqrt[3]{D}) \tag{2}$$

(μ' is a constant varying with the liquid under consideration) has been thoroughly tested by him, and found to be in excellent agreement throughout with the thermodynamical equation for all normal liquids. For its theoretical significance reference must be made to the original papers.

A third formula, proposed by Dieterici:[4]

$$L = 0.0431833 \ P \ (V — v) — 4.577 \ c \ (T/M) \log (d/D) \tag{3}$$

(c is a constant varying with the liquid) has also been examined by Mills.[2] It is found to be consistently inaccurate at low temperatures, although

[1] Internal + external, at constant temperature T

[2] Mills, Loc. cit.

[3] Mills, J. Phys. Chem, 6, 209 (1902); 8, 383 and 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132 and 594 (1907); 13, 512 (1909); 15, 417 (1911); 18, 101 (1914).

[4] Dieterici, Ann. Physik, 25, 569 (1908).

the agreement at higher temperatures is remarkably good   A similar equation was previously suggested by Crompton [1]

Kleeman[2] has deduced mathematically, from assumptions regarding molecular attraction, the equation

$$L = 0.0431833 \, P \, (V - v) - K \, (d^2 - D^2) \tag{4}$$

(K is a constant varying with the liquid)   The same equation has also been put forward by Batschinski [3]

The present author[4] has shown that the following simple relation holds

$$I = k(I_c - T)^n \tag{5}$$

(k is a constant varying with the liquid, n is for all normal liquids equal to 0.386)   Later investigation showed that the above is an interpolation formula, and is dependent upon the two equations

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1(T_c - T)^{1/2}$$

$$\sqrt[3]{d_c} - \sqrt[3]{D} = k_2(T_c - T)^{1/2}$$

which were demonstrated to hold satisfactorily for normal liquids   By combining these equations with that of Mills (Equation 2 above) we obtain

$$K = 0.0431833 \, P \, (V - v) + k_1\mu'(I_c - I)^{1/2} + k_2\mu'(I_c - I)^{1/2} \tag{5a}$$

This is the more correct expanded form of Equation 5 above   The first part of the equation represents the external heat of vaporization, which is variable in magnitude, but at most temperatures is comparatively small, the exponent $n = 0.386$ in Equation 5 is, consequently, intermediate between the two simple values (one third and one-half) in Equation 5a   For associated liquids the equation still holds if the value of n is modified [5]

Tyrer[6] has recently proposed a somewhat similar formula

$$I = 0.0431833 \, P \, (V - v) + C(I_c - I)^{1/2}/(d^{1/4} + D^{1/2}) \tag{6}$$

C is a constant varying with the liquid under examination

Applebey and Chapman[7] have deduced the relation

$$I = RT \log_e (V - b)/(v - b) + RT^2[1/(v - b) + 1/(V - b)] \, db/dI \tag{7}$$

[1] Crompton, *Proc Chem Soc*, **17**, 61 (1901)

[2] Kleeman, *Phil Mag*, [6] **20**, 665 (1910)   A somewhat different formula was advanced in a previous paper, *Phil Mag*, [6] **19**, 795 (1910)

[3] Batschinski, *Ann Physik*, **14**, 288 (1904)

[4] Kendall, *Meddel från K Vet Akads Nobelinstitut*, Band 2, No 29 (1912),   The Properties of Liquids as Functions of the Critical Constants "   Since this paper is not generally available, the significance of the equation is briefly indicated above

[5] Kendall, *Meddel från K Vet Akads Nobelinstitut*, Band 2, No 36 (1913), "The Heat of Vaporization of Associated Liquids "

[6] Tyrer *J Phys Chem*, **17**, 717 (1913)

[7] Applebey and Chapman, *J Chem Soc* **105**, 734 (1914)   The equation in the original paper, is referred to molecular volumes   These are here changed to V and v (volume of 1 g)   The constant b in 7 is consequently the usual van der Waals' constant divided by M (mol wt)   The same holds for equation 10

in which b (the constant of van der Waals' equation) is assumed to vary linearly with the temperature. Methods for the determination of b_c (the value of b at the critical temperature) and db/dT are developed; when these quantities are known, L can be evaluated.

Rodzewitz[1] has recently put forward the equation:

$$L = 0.0431833 \ KT^2 \{(P_c - P)/P\} . (dP/dT) \tag{8}$$

(K is a constant varying with the liquid.)

The validity of this equation depends on that of the relation:

$$(V - v) = KT(P_c - P)/P$$

On examination, however, it is found that, while the above relation is approximately true at low temperatures (as the figures given by Rodzewitz show), yet it fails entirely at temperatures approaching the critical point. This will be evident from the following tabulation where the results for octane and carbon tetrachloride are shown ·

t.	80	100	120	140	160	180	200	220	240	260	280
100 K(CCl$_4$)	1.16	1 15	1 15	1.16	1.19	1.21	1.26	1 35	1.54	1 99	6.44
100 K(octane)			2.79	2 81	2 83	2.85	2.90	3 04	3.28	3.83	5.52

The equation can, therefore, be employed only at low temperatures. The same is true of the general equation of Arrhenius ·[2]

$$L = A_0 - CT^2 \tag{9}$$

where A_0 and C are constants dependent on the liquid. Similarly, the formula of Bakker:[3]

$$L = RT \log_e (V - b)/(v - b) \tag{10}$$

although directly deduced from the equation of van der Waals, is not in agreement with the results of experiment. Finally, there may be mentioned the equation of McLewis ·[4]

$$L = (T/\alpha)(d/\beta) \tag{11}$$

(α = coefficient of expansion, β = compressibility) which gives approximate agreement with the experimental values for the few cases where data for normal liquids are available.

It will be seen that most of the above equations contain a constant dependent upon the liquid under consideration. It is usually possible to remove this, and so generalize the equation, by combination with the rule of Trouton or some similar law. Thus equation 5 becomes:

$$ML = 20.7 \ T_c(1 - T/T_c)^n \tag{5b}$$

a relation perfectly general for all normal liquids. Since, however, the rule of Trouton is only approximately correct, such equations will not

[1] Rodzewitz, *J. Russ. Phys. Chem. Soc., Phys.* **45**, 355 (1914).

[2] Arrhenius, *Meddel från K. Vet -Akads. Nobelinstitut,* Band **2**, No. 8 (1911).

[3] Bakker, *Z. Physik. Chem.,* **18**, 519 (1895).

[4] McLewis, *Phil. Mag.,* [6] **22**, 268 (1911).

usually reproduce the experimental values sufficiently closely to be of ' practical utility.

In the following tables only those equations (2 to 7, inclusive) are compared with the thermodynamical Equation 1 which are applicable throughout the whole of the available experimental range   The constants employed are shown in Table I, values not tabulated previously, and calculated by the present author, are indicated by a star.   The collected results are given in Tables II–V; divergences from the experimental values

TABLE I - CONSTANTS OF EQUATIONS

		Octane	Methyl butyrate	Carbon tetrachloride	Fluorobenzene
T_c		569 2	554 25	556 15	559 55
μ'	(Mills)	93 16	91 31	44 01	85 65
c	(Dieterici)	1 858	1 824	1 667	1 711
K	(Kleeman)	176 2	113 3*	19 74	8' 44
k	(Kendall)	9 72	10 47	5 92	10 04
C	(Tyrer)	134 4*	140 8*	133 0*	146 0*
b_c	(Applebey)	190 63	131 74	107 54	105 85
db/dt	(Applebey)	0 11732	0 08459	0 06674	0 06472

TABLE II —OCTANE   HEATS OF VAPORIZATION

t	Ther	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	89 46	85 69	97 63	95 69	87 49	89 83	
120	71 43	71 83	73 05	73 37	71 56	72 38	73 82
140	68 28	68 61	69 36	69 36	68 28	68 83	
160	64 75	65 06	65 52	65 31	64 79	64 96	
180	60 91	61 14	61 40	60 90	60 93	60 85	59 57
200	56 61	56 72	56 89	56 15	56 64	56 38	
220	52 03	51 80	51 83	50 98	51 81	51 39	
240	45 97	45 72	45 63	44 76	46 02	45 57	42 92
260	39 14	38 63	38 46	35 75	38 85	38 61	
280	28 26	28 17	27 85	27 55	28 50	28 69	25 96
290	19 10	19 50	19 12	19 20	19 35	20 34	17 87

TABLE IIa —OCTANE   DIVERGENCES

t	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	−3 77	+8 17	+6 23	−1 97	+0 37	
120	+0 40	+1 62	+1 94	+0 13	+0 95	+2 39
140	+0 33	+1 08	+1 08	0 00	+0 55	
160	+0 31	+0 77	+0 56	+0 04	+0 21	
180	+0 23	+0 49	−0 01	+0 02	−0 06	−1 34
200	+0 11	+0 28	−0 46	+0 03	−0 23	
220	−0 23	−0 20	−1 05	−0 22	−0 64	
240	−0 25	−0 34	−1 21	−0 05	−0 40	−3 05
260	−0 51	−0 68	−1 39	−0 29	−0 53	
280	−0 09	−0 41	−0 71	+0 24	+0 43	−2 30
290	+0 40	+0 02	+0 08	+0 25	+1 24	−·1 23
Av (120–280°)	0 27	0 65	0 93	0 11	0 44	2 13

are shown in Tables IIa–Va. In the calculation of the "average diver-
gence," the figures for 0° and for temperatures within 10° of the critical
are disregarded.[1]

TABLE III —METHYL BUTYRATE   HEATS OF VAPORIZATION

t	Ther	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	95 79	90 91	101 88	101 17	92 35	95 08	
100	77 80	7813	79 58	80 41	77 95	79 02	
120	74 31	74 72	75 58	76 10	74 48	75 17	80 79
140	70 84	71 04	71 61	71 62	70 77	71 13	
160	66 53	66 87	67 08	66 87	66 69	66 77	65 88
180	62 00	62 26	62 45	61 79	62 26	62 01	
200	57 41	57 19	57 31	56 43	57 18	56 86	55 20
220	51 31	51 07	51 08	50 23	51 28	50 83	
240	44 14	43 69	43 61	42 70	44 00	43 74	
260	34 44	34 06	33 85	33 26	34 10	34 25	32 00
280	11 16	11 98	11 64	12 42	11 59	12 62	11 77

TABLE IIIa —METHYL BUTYRATE   DIVERGENCES

t	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	−4 88	+6 09	+5 38	−3 44	−0 71	
100	+0 33	+1 78	+2 63	+0 15	+1 22	+2 99
120	+0 41	+1 27	+1 89	+0 17	+0 86	
140	+0 20	+0 77	+0 78	−0 07	+0 29	
160	+0 34	+0 55	+0 34	+0 16	+0 24	−0 65
180	+0 26	+0 45	−0 21	+0 26	+0 01	
200	−0 22	−0 10	−0 98	−0 23	−0 55	−2 21
220	−0 24	−0 23	−1 08	−0 03	−0 52	
240	−0 45	−0 53	−1 44	−0 14	−0 40	
260	−0 38	−0 59	−1 18	−0 34	−0 19	−2 44
280	+0 82	+0 48	+1 26	+0 43	+1 46	+0 61
Av (100–260°)	0 31	0 70	1 19	0 17	0 48	2 00

TABLE IV —CARBON TETRACHLORIDE   HEATS OF VAPORIZATION

t	Ther	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	51 87	52 40	54 13	56 14	52 36	53 62	
80	46 00	46 44	46 11	47 41	46 03	46 60	
100	44 15	44 58	44 20	45 16	44 23	44 58	44 33
120	42 08	42 54	42 18	42 75	42 30	42 44	
140	39 92	40 36	40 11	40 35	40 22	40 21	
160	37 95	38 08	37 99	37 92	37 95	37 86	38 38
180	35 40	35 46	35 47	35 22	35 43	35.25	
200	32 61	32 52	32 67	32 18	32 62	32 39	
220	29 45	29 14	29 35	28 77	29 33	29 13	29 72
240	25 56	25 10	25 35	24 76	25 33	25 24	
260	20 07	19 70	19 89	19 49	19 90	20 05	
280	10 43	10 45	10 48	10 48	9 22	10 29	10 71

[1] Applebey and Chapman have calculated all results (except for fluorobenzene) at
intervals of 30° In the tables their figures for intermediate temperatures are omitted
to economize space, but for the final calculation of "average divergences" all results
within the temperature range indicated above have been taken into account

TABLE IVa —CARBON TETRACHLORIDE   DIVERGENCES

t	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	+0 53	+2 26	+4 27	+0 49	+1 75	
80	+0 44	+0 11	+1 41	+0 03	+0 60	
100	+0 43	+0 05	+1 01	+0 08	+0 43	+0 18
120	+0 46	+0 10	+0 67	+0 22	+0 36	
140	+0 44	+0 19	+0 43	⊢0 30	+0 29	
160	+0 13	+0 04	—0 03	0 00	—0 09	+0 43
180	+0 06	+0 07	—0 18	+0 03	—0 15	
200	—0 09	+0 06	0 43	+0 01	—0 22	
220	—0 31	—0 10	—0 68	0 12	—0 32	+0 27
240	—0 46	—0 21	0 80	—0 23	—0 32	
260	—0 37	—0 18	—0 58	—0 17	—0 02	
280	+0 02	+0 05	+0 05	—1 21	—0 14	+0 28
Av (80–260°)	0 32	0 11	0 62	0 12	0 28	0 28

TABLE V —FLUOROBENZENE   HEATS OF VAPORIZATION

t	Ther	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	87 78	88 39	93 51	94 80	89 14	91 44	
80	80 07	79 11	79 53	80 56	78 60	79 99	79 76
100	77 10	76 11	76 19	76 79	75 59	76 48	77 21
120	73 03	72 69	72 55	72 80	72 34	72 80	73 1
140	68 75	69 00	68 79	68 71	68 84	68 91	69 27
160	64 37	64 99	64 79	64 45	64 97	64 81	65 39
180	60 17	60 65	60 55	59 91	60 87	60 41	61 08
200	55 35	55 79	55 78	54 91	56 16	55 63	55 8
220	50 37	50 36	50 51	49 41	50 73	50 27	50 34
240	44 07	43 80	43 97	43 00	44 22	43 87	43 77
260	35 65	35 32	35 43	34 70	35 60	35 64	35 21
280	20 82	21 16	21 07	20 17	20 74	21 60	19 95

TABLE Va — DIVERGENCES

t	Mills	Dieterici	Kleeman	Kendall	Tyrer	Applebey
0	+0 61	+5 73	+7 02	+1 36	+3 66	·
80	—0 96	—0 54	+0 49	—1 47	—0 08	—0 31
100	—0 99	—0 91	—0 31	—1 51	—0 62	+0 11
120	·0 34	- 0 48	—0 23	—0 69	—0 23	+0 21
140	+0 25	+0 04	—0 04	+0 09	+0 16	⊢0 52
160	+0 62	+0 42	+0 08	+0 60	+0 44	⊣1 02
180	+0 48	+0 38	—0 26	+0 70	+0 24	+0 91
200	+0 44	+0 43	—0 44	+0 81	+0 28	+0 49
220	—0 01	+0 14	—0 96	+0 36	—0 10	—0 03
240	—0 27	—0 10	—1 07	+0 15	—0 20	—0 30
260	—0 33	—0 22	—0 95	—0 05	—0 01	—0 44
280	+0 34	+0 25	—0 65	—0 08	+0 78	—0 87
Av (80–260°)	0 47	0 37	0 48	0 64	0 24	0 43

In the discussion of the above figures, Tables II IV will be considered first, since the results obtained are essentially the same throughout.

Table V (fluorobenzene) gives results of a different nature, requiring fur
ther investigation, it is, therefore, dealt with subsequently.

From the results obtained with octane, methyl butyrate and carbon
tetrachloride, it is evident that the equations of Kendall and of Mills
afford values most consistent with the experimental figures   The di-
vergences are always small, except at 0° and near the critical point, where
the experimental values are liable to error   Even at these temperatures
the divergences are usually smaller than those obtained with the remain-
ing formulas   The equations of Kleeman and of Dieterici (and, to a
smaller degree, that of Tyrer) are not so accurate, and lead to values at
the lowest temperatures which are consistently too high   The equation
of Applebey and Chapman gives values differing fairly considerably from
the experimental   It must be mentioned, however, that the effect of
small experimental errors upon the calculated values is much greater
here than in any of the other equations

The final table for fluorobenzene shows exactly the opposite results
The equations of Kendall and of Mills here give the poorest agreement
with the experimental data   (Kleeman's values may be appreciably
improved by a slight modification in the value of the constant employed
by him)   Also, for practically all of the formulas, the calculated values
at the lowest temperatures (80–120°) are uniformly too low

This difference in behavior may be satisfactorily explained by a considera
tion of the experimental data   It is found on examination that the values
for fluorobenzene at low temperatures are affected by errors of observation

The method employed for illustrating this is as follows   The function
dI/dT is plotted against temperature   Now, in all normal curves, the
heat of vaporization, after a rapid increase with decreasing temperature
near the critical point, increases more and more slowly as temperature is
further lowered   When the rate of this increase (dL/dI) is plotted against
I, therefore, we obtain a smooth curve, with rapid change of slope near
the critical temperature, but approximating more nearly to a straight
line at lower temperatures   The values for dL/dT will decrease contin-
uously, but more and more slowly, as temperature falls

The results for the lower temperatures are shown in the accompanying
diagram   The values for dL/dI are found, at intervals of 20°, by inter
polation from the preceding tables, e g , for octane at 130°, $dL/dT =$
$1/20 (L_{120} - L_{140})$ It is evident that, while the results for octane and
carbon tetrachloride lie fairly closely upon smooth curves of the required
type, the values obtained in the case of fluorobenzene show considerable
fluctuations [1]   The experimental data in this case are clearly inconsistent,

[1] The values for methyl butyrate are not plotted to avoid confusion in the diagram
The curve is almost identical with that for fluorobenzene   The agreement in this case
is not quite so good as with octane or carbon tetrachloride

and a repetition of the observations would probably lead to results in agreement with those obtained from other liquids, *i. e.*, exhibiting close concordance with Equations 2 and 5.
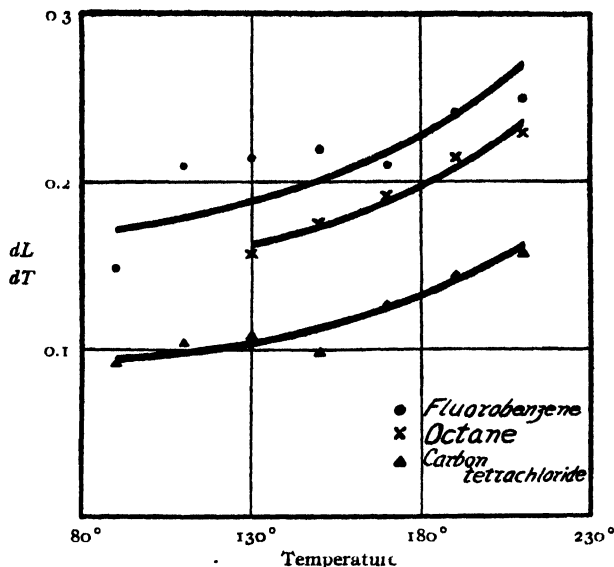
It is in this direction— the correction of the experimental data—that the equation of Mills has already repeatedly proved itself to be of service. Large divergences were existent between the original experimental values of Young and the calculated values of Mills for several liquids. It was invariably found, when the observations were repeated, that the *experimental values* were in error.[1]

The utility of the various equations proposed will probably be restricted, for the present, to this practical application. It is hard to conceive how much ·progress can be made on the theoretical side until the fundamental points at issue are settled. For the most obvious conclusion to be drawn from the present investigation is that the heat of vaporization is a quantity which is peculiarly adaptable to representation by empirical formulas. It is impossible that all of the equations considered can be of theoretical significance. Were this the case, an army of physicists might devote their lives to tabulating the different relations, between the quantities concerned, obtainable by the combination and recombination of these equations.[2] It will be evident, however, that the fact that a formula,

[1] Mills, *Phil. Mag.*, [6] 21, 84 (1911); 24, 483 (1912).

[2] From three equations alone, Mills obtained thirty-six new relations (THIS JOURNAL 31, 1099 (1909)). The number possible soon increases to billions as more equations are introduced. (Compare Bridgman, *Phys. Rev.*, 3, 273 (1914))

in this field, fits the experimental results is no confirmation, taken alone, of the truth of the principles involved.

Further approximate or empirical relations will consequently be super-fluous, so long as the fundamental theoretical principles of the subject remain indefinitely outlined. The rigorous mathematical development of the laws of molecular attraction—a field in which Mills has already performed valuable pioneer work—is the necessary prerequisite to any real progress.

Summary.

The accuracy of the various equations proposed for representing heats of vaporization has been tested by comparison with the experimental data of Young. In three out of the four cases examined, the equations of the author and of Mills afford most satisfactory agreement. In the remaining case the experimental figures are shown to be inaccurate.

It has been pointed out that the heat of vaporization is a quantity so adapted to representation by different formulas that no conclusions can be drawn as to their relative theoretical merits. At present, the equations are useful only as checks upon the experimental data.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
   COLUMBIA UNIVERSITY, NEW YORK CITY.

THE POTENTIAL OF SILVER IN NONAQUEOUS SOLUTIONS OF SILVER NITRATE.[1]

BY VERNETTE L. GIBBONS AND F. H. GETMAN.
Received June 1, 1914

1. Introduction: (a) Aim of the Investigation; (b) Preparation of Materials. 2. Measurements of Electrical Conductance. 3. Determination of Transport Numbers 4. Determination of the Electromotive Force of Various Concentration Cells. 5 Discussion of Results. 6. Summary. 7 Chronological Bibliography.

1. Introduction.

The study of the potentials of metals in nonaqueous solutions of their salts was begun by Campetti[2] about twenty years ago. Since, however, the drop electrode was employed in these experiments the results cannot be considered trustworthy.

A few months later, Jones[3] published results of measurements of the combinations

$$Ag \mid AgNO_3 \text{ in solvent I} \mid AgNO_3 \text{ in solvent II} \mid Ag.$$
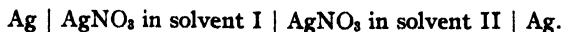
The solvents used were water, ethyl alcohol, methyl alcohol and acetone.

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[1] A Dissertation presented to the Faculty of Bryn Mawr College by Vernette L. Gibbons in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Atti accad. Torino*, **28**, 61 and 228 (1893).

[3] *Z. physik. Chem.*, **14**, 346 (1894).

The concentrations of both solutions were identical for each individual experiment. Electromotive forces of considerable numerical value were obtained, but they varied with the combination employed. He concluded that the solution tension of silver depends upon the nature of the solvent in which the salt is dissolved.

Kahlenberg[1] carried out a long series of investigations of the behavior of ten different metals, in solutions of their salts in about thirty different solvents. He measured the potential of silver in o.1 N solutions of silver nitrate in twenty-four different solvents. The silver nitrate solution formed one part of the cell, and in each case the other part was either a normal or o.1 N calomel electrode. The metals dipped into solutions contained in test tubes or open beakers and the connection between the two vessels was made by means of a strip of filter paper folded to several thicknesses. Thus the solutions were liable to change in concentration because of evaporation or of absorption of moisture from the atmosphere. The difference of potential at the junction of the two liquids was neglected and no definite temperature was maintained. The change in electromotive force caused by the interaction of the ions of the two electrolytes at the junction was entirely overlooked.

The following year Kahlenberg[2] measured the electromotive force of concentration cells of silver nitrate in pyridine and acetonitrile. He compared the results with the values calculated by means of the Nernst equation

$$E = \frac{RT}{nF} \log_e \frac{m_1\Lambda_1}{m_2\Lambda_2},$$ (1)

assuming that the potential at the junction between the two solutions was negligible. Although a fair agreement between experimental and calculated values had been obtained when aqueous solutions were used, here an utter lack of agreement was found, and he was forced to the conclusion that the formula was not applicable to cells involving nonaqueous solutions.

In a later article, Kahlenberg[3] gave the results of measurements of the electromotive force of the system

Ag | o.1 N AgNO$_3$ in water | o.1 N AgNO$_3$ in pyridine and water | Ag.
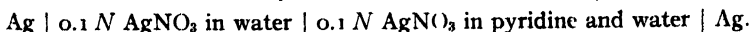
He found that, by increasing the amount of water in the mixed solvent, the electromotive force of the cell diminished, and he concluded that the potential difference between silver and silver nitrate depended upon the composition of the solvent.

Carrara and D'Agostini,[4] from their investigation of concentration cells

[1] *J. Phys. Chem.*, **3**, 379 (1899).
[2] *J. Ibid.*, **4**, 709 (1900).
[3] *Z. Elektrochem* , **11**, 385 (1905).
[4] *Atti R. Ist. Veneto*, **62**, 793 (1902).

in methyl alcohol, concluded that in this solvent the Nernst formula was applicable.

In 1905, Carrara[1] turned his attention to the influence of the solvent upon the solution pressure of the metals. He found that in methyl alcohol this pressure was less than in water and was, therefore, not independent of the nature of the solvent.

Sackur[2] criticized the work of Kahlenberg and also that of Carrara and D'Agostini. He maintained that neither had disproved the applicability of Nernst's law; that, in fact, in the case of the work of Carrara and D'Agostini the results with three out of the four metals investigated could be interpreted as in full accord with that law.

In the same year, Bjerrum[3] attempted to eliminate the diffusion potential at the junction of the two liquids by using a concentrated solution of potassium chloride as a "middle liquid" and obtained values more nearly constant for each experiment and with less variation in a series of experiments than when this "middle liquid" was not used.

The measurement of the electromotive force of concentration cells of silver nitrate in methyl- and ethylamine was undertaken by Bodländer and Eberlein[4] as a means of studying the complexes formed in these solvents. They considered that these ions are represented by the formulas, $Ag(CH_3NH_2)_2$ and $Ag(C_2H_5NH_2)_2$, thus showing the similarity of these solvents to ammonia.

The potential difference of concentration cells with liquid ammonia as a solvent was measured by Cady in 1905.[5] His conclusion was that the Nernst formula could be used to calculate the electromotive force when this solvent was used in the cells.

A large amount of experimental work was carried out by Neustadt and Abegg[6] for the purpose of determining the relation of the tension series of the metals to the solvent. $Ag \mid AgNO_3$ was always made one-half of the cell. In only a few cases is mention made of the use of a "middle liquid;" although, in several cases, the solution in the second half of the cell was a chloride. They concluded that the tension series was quite independent of the solvent. The liquid potentials in a given system were considered at some length but without reaching any definite conclusion.

The behavior of cadmium in alcoholic solutions of its salts was investigated by Getman.[7] He measured the electromotive force of the metal in different concentrations of its salts, the other half of the cell being in

[1] Gass. chim. ital., 35, I, 132 (1905).
[2] Z. Elektrochem., 11, 385 (1905).
[3] Z. physik. Chem., 53, 428 (1905).
[4] Ber., 36, 3945 (1903).
[5] J. Phys. Chem., 9, 476 (1905).
[6] Z. physik. Chem., 69, 486 (1909)
[7] Am. Chem. J., 46, 117 (1911).

each case a normal calomel electrode.   The changes in potential with concentration in the alcoholic solutions were found to be opposite to the change in aqueous solutions, *i. e.*, the potential of cadmium became more strongly negative with increasing concentration of the solutions of its salts.   The electromotive force developed at the junction of the two solutions was assumed to be negligible.   The possibility of the application of Nernst's equation to such nonaqueous solutions was considered doubtful.

In 1912 the potentials of zinc in alcoholic solutions of zinc chloride were measured by Getman and Gibbons,[1] one-half of the cell being in each case the normal calomel electrode.   It was found that the potentials of zinc in solutions in ethyl alcohol became more strongly negative with increasing concentration of the solutions.   This was the same effect observed by Getman in his study of solutions of cadmium salts.   Solutions in methyl alcohol showed fluctuations of potential of more than ten millivolts, an effect which is to be studied further.   Shortly after this, Dr. Laurie of Edinburgh, in a personal letter to one of us, called attention to the fact that the potential difference developed at the junction of the two liquids might sometimes have considerable influence.[2]

Roshdestwensky and Lewis[3] have studied concentration cells of silver nitrate in acetone.   They not only measured the electromotive forces of various combinations of freshly prepared solutions, but they made similar measurements both with solutions which had stood for six weeks in the dark and with solutions which had stood one day exposed to the sunlight.   The agreement of the results in all cases is within the limits of experimental error.   The type of cell used was not described, but the two solutions were in direct contact, thus possibly developing a potential difference at the junction.   In the following way, however, this potential difference was shown to be very slight.   A solution of 0.01 N silver nitrate was interposed as a "middle liquid" and the measurements repeated. The results agree with those for a similar cell without this "middle liquid." Therefore, assuming Nernst's law to be valid for these systems, Roshdestwensky and Lewis calculated the transport numbers for the ions and found that in solutions ranging in concentration between the limits of 0.02 0.007 N the value for the anion lay between 0.60 and 0.58, and for more dilute solutions (0.007 0.0005 N) the value was 0.56.   As a result of further attempts to eliminate the potential differences at the junction of the two liquids, they concluded that the validity of "middle" liquid methods for acetone solutions was doubtful since, in all cases, where an effect was observed there was an increase instead of a decrease of electromotive force.

[1] *Am. Chem. J.*, **48**, 124 (1912).

[2] *Proc. Roy. Soc. Edinb.*, **31**, 375 (1911).

[3] *J. Chem. Soc.*, **101**, 2094 (1912).

Measurements of the electromotive force of silver nitrate concentration cells with water and ethyl alcohol as solvents were carried out by Bell and Feild.[1] They used a closed apparatus of a U form, having an outlet tube in the middle, closed with a three-way stopcock, so that the two arms could be connected with each other or the solution drawn from either one without disturbing that in the other. In this way, the solutions could be brought to the same level in both sides of the tube without intermingling and could be kept separated except during the time of actual measurement. Apparently, the effect of gravity in causing inter-diffusion was overlooked. Writing Nernst's law in the form

$$\frac{E}{\log_{10} C_1/C_2} = \frac{2v}{u+v} \frac{RT}{NF} \log_e 10 = K, \tag{2}$$

they obtained from the data for concentration cells in water, values for K that vary from 0.0560 to 0.0623. Taking the latter as the value of K they calculated the value of v in the above formula and found it to be 0.523 instead of 0.528 as given by Lehfeldt.[2] Since the values of v are probably smaller in more concentrated solutions, K will, of course, for such solutions, be proportionately smaller. In the same way, K was calculated from the measurements of the electromotive forces of concentration cells in ethyl alcohol and, since K varied, they assumed that the migration ratios were not constant. The value of v calculated from the highest value of K obtained was 0.62.

Bjerrum[3] sought to eliminate the potential at the junction by using, in one experiment, a saturated, and in another, a half-saturated solution of potassium chloride as a "middle liquid." By comparing the results of the two measurements and by extrapolating, he concluded that better results were obtained than when the potassium chloride solution was not present.

Cumming and Abegg[4] concluded that a saturated ammonium nitrate solution formed an exceptionally good "middle liquid" for eliminating the potential at the junction.

Thermodynamic principles were applied by Henderson[5] in the derivation of the following equation for calculating the potential developed between two aqueous solutions:

$$E = \frac{RT}{F} \frac{(u_1-v_1)C_1 - (u_2-v_2)C_2}{(u_1W_1 + v_1W_1)C_1 - (u_2W_2 + v_2W_2)C_2} \log_e \frac{(u_1W_1 + v_1W_1)C_1}{(u_2W_2 + v_2W_2)C_2} \tag{3}$$

[1] This Journal, **35**, 715 (1913).

[2] *Electrochemistry*, p. 256 (1904).

[3] *Z. physik Chem.*; **53**, 49 (1905).

[4] *Z. Elektrochem.*, **13**, 17 (1907).

[5] *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

C_1 and C_2 represent equivalent concentrations. u_1, v_1, u_2, v_2 represent absolute ionic velocities W_1, $\overline{W}_1$, W'_2, W_2 represent the valences of the ions.

Subsequent investigations by Bjerrum[1] led him to conclude that, if the electromotive force remained constant for some minutes after contact between the liquids had been established, the effect of diffusion was negligible and Henderson's formula could be applied   He found, also, that if the connection between the two parts of the cell was made through a layer of sand much more constant results were obtained   In a second paper,[2] he showed that ammonium nitrate gave less satisfactory results than potassium chloride when used as a "middle liquid," but that it might be used in cases where the latter would give rise to chemical action   He also showed that the values obtained by extrapolation, when a solution of potassium chloride was used, agreed closely with those computed by means of Henderson's formula, and that, if the degree of dissociation was calculated by means of Nernst's equation, the result did not at all agree with the value obtained by calculation from conductance measurements

The electrode and liquid potentials of nonaqueous solutions were studied by Isgarischew[3] who applied Henderson's formula to methyl alcohol solutions   He referred all his measurements to the normal hydrogen electrode as a standard   He prepared a calomel electrode in methyl alcohol, determined its electromotive force and, with the aid of this electrode calculated the electrode potential of several metals   Certain metals he found showed great tendency to become passive   The electrode potential of silver was obtained by using as one-half of the cell a $Cd \mid Cd(NO_3)_2$ electrode which had been measured against the calomel electrode   Since the potential of this cadmium electrode showed a tendency to increase quite rapidly at first, the two half cells were not placed in contact until a constant value had been obtained for the electromotive force of this electrode.

Isgarischew[4] made a further study of the passivity of metals and concluded that the phenomenon was caused by oxidation   In the case of copper, however, instead of an oxide, a complex compound of copper chloride and alcohol was formed on the surface of the metal   He measured the electromotive force of the combination

$$Ag \mid AgNO_3 \text{ in methyl alcohol} \mid AgNO_3 \text{ in water} \mid Ag,$$
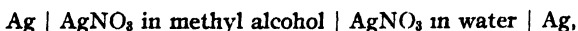
and computed the liquid potential by means of Henderson's formula, obtaining an electrode potential much larger than when the cadmium electrode was used   He sought to measure similar combinations of ethyl

[1] Z Elektrochem   17, 58 (1911)
[2] Ibid , 17, 388 (1911)
[3] Ibid , 18, 568 (1912)
[4] Ibid , 19, 491 (1913)

alcohol and aqueous solutions, and stated that it was impossible to apply Henderson's formula to compute the liquid potential of such combinations, but gave no reasons for this conclusion.

The following simplification of Henderson's formula has recently been given by Cumming:[1]

$$E = \frac{RT}{F} \cdot \frac{K(2n-1) - K'(2n'-1)}{KW_1 - K'W_2} \log_e \frac{KW_1}{K'W_2} \qquad (4)$$

K and K' are the specific conductances, N and N' the migration ratios and W_1 and W_2 the corresponding valences. This equation requires only data that can be determined experimentally; and, if it is assumed that the migration ratios in the two solutions are the same, the equation becomes identical with Nernst's equation. Cumming applied the equation to the results of Bjerrum and others on the potentials of various chloride solutions with calomel electrodes and obtained satisfactory values.

Since the experimental work to be described in the following pages was completed, Cumming and Gilchrist[2] have published a method for ascertaining the true values for the diffusion and electrode potentials from the observed potential of the cell. They conclude that a new boundary must be made shortly before the measurement is taken, and that capillary tubes must be avoided in the construction of an electromotive force cell.

Thus, as we have seen, considerable work has been done, especially within the last three years, upon the subject of the potentials of metals in aqueous and nonaqueous solutions of their salts. Many of these measurements have been made with open cells connected by capillary tubes, filter paper or sand, with "middle liquids" whose effect is more or less uncertain, or with closed cells, no attempt being made to calculate the potential at the junction between the solutions. It has, therefore, been considered advisable to carry out an investigation of the behavior of silver in nonaqueous solutions of silver nitrate. This combination was chosen because silver nitrate can be obtained and kept in a state of great purity. It is also soluble in a large variety of solvents. In some of these solvents it might be expected, from conductance measurements, that abnormal effects would be observed.

The development of the Cumming equation has made it possible to compute the potential at the junction of the two liquids from purely experimental data, and has thus removed one source of error.

The apparatus employed for the electromotive force measurements was free from the defects mentioned by Cumming and Gilchrist and embodied several improvements over the ordinary type of cell. The investigation divides itself into three parts as follows:

[1] *Trans. Faraday Soc.*, **8**, 86 (1913).

[2] *Ibid.*, **9**, 174 (1914).

I. The measurement of the conductance of the solutions employed.

II. The determination of the transport numbers in as many of these solutions as possible.

III. The measurement of the electromotive force of various concentration cells in each solvent, and the determination of the electromotive force of the following combinations

Ag | o.1 or o o1 N AgNO₃ in water | o 1 or o o1 N AgNO₃ in solvent II | Ag

Preparation of Materials —The silver nitrate used in making up the solutions was finely powdered and kept in a desiccator over phosphorus pentoxide

The ethyl alcohol (high-grade commercial "Absolute" 99 6%) was dehydrated over lime ('aus Marmor") for several weeks It was then distilled, using a fractionating column, and the distillate was collected in a receiver protected from the moisture and gases of the atmosphere by means of a tube filled with soda lime The boiling point was 78 8° at 757 4 mm of mercury

The methyl alcohol was subjected to the same treatment as the ethyl alcohol. The fraction boiling between 64 3° and 64 8° at 746 mm of mercury was collected for use

The acetone was dried over fused calcium chloride, distilled, allowed to stand over anhydrous copper sulfate several weeks, then redistilled and the fraction boiling between 56° 56 1° was collected Its conductance was so slight it could not be measured

Commercial aniline, was distilled, allowed to stand over fused potassium carbonate several days, then redistilled using a fractionating column. The distillation was repeated until a nearly colorless distillate was obtained which boiled between 181 5°-182° at 751 8 mm of mercury. The conductance was too slight to be measured

The pyridine, of the best grade obtainable, was treated with fused potassium hydroxide for several days, filtered and after repeated fractionations the portion boiling between 114° 116° at 742 mm of mercury was collected

The water used was distilled according to the method of Jones and Mackay. It was collected in a bottle well protected from the gases of the atmosphere.

2. Electrical Conductance.

All measurements were made at 25° The thermostat consisted of two concentric galvanized iron tanks, the annular space between them being filled with sawdust. The water was well stirred and was heated by means of an incandescent lamp that had been coated with a ruby varnish to prevent the reducing action of light on the silver nitrate solutions. The temperature was maintained constant at 25 ± 0.05° by means of an electrically controlled Ostwald thermoregulator.

The mother solution in each solvent was made up by direct weighing, and the more dilute solutions were made from this by means of carefully calibrated burets and flasks.

The measurements of electrical conductance were made by means of the well-known Kohlrausch apparatus, a Leeds and Northrup cylindrical bridge being used. The cells were of two types. The ordinary Arrhenius form closed by a tight-fitting ebonite cover was used for most of the work, but the form described by Kreider and Jones[1] having a ground glass stopper and concentric cylindrical platinum electrodes, was used for the solutions in ethyl alcohol. The constants of these cells were determined by means of a potassium chloride solution containing one mol of the salt in 128 liters of water. Its equivalent conductance was taken as 142.4 at 25°. The cell constants were redetermined frequently during the investigation and were found to remain practically constant. The average value for the Arrhenius type of cell was 16.83 and for the Kreider and Jones type 2.63. The electrodes of the cell were platinized in the usual manner. After each measurement, the cell and electrodes were carefully cleansed, rinsed first with distilled water, then several times with absolute ethyl alcohol and dried in a current of pure dry air.

The cell was allowed to stand in the thermostat for twenty or thirty minutes and the contents were thoroughly stirred to insure a uniform temperature before a measurement was taken. From three to six readings were taken for each dilution. The cell was allowed to stand twenty minutes longer in the thermostat and the readings repeated If the two sets of readings did not agree, the cell was freshly filled and another set of readings taken for comparison. Tables I to V give the results of these measurements.

TABLE I —SILVER NITRATE IN ETHYL ALCOHOL		
m	V	$\Lambda_m°$
0 1	10 0	10 81
0 01	100 0	22 06
0 0078	128 4	23 72
0 003	333 3	28 14
0 001	1000 0	34 95
0 00056	1786 0	37 79
0 0003	3333 3	38 52
0 0001	10000 0	40 71

TABLE II.—SILVER NITRATE IN METHYL ALCOHOL		
m	V	$\Lambda_m°$
0 1	10 0	36 64
0 01	100 0	68 75
0 006	166 7	74 88
0 003	333 33	83 14
0 0012	833 3	87 30
0 001	1000 0	90 10
0 0003	3333 3	87 82
0 0001	10000 0	73 23

TABLE III —SILVER NITRATE IN ACETONE		
m	V	$\Lambda_m°$
0 01	100 0	10 51
0 003	333 3	11 39
0 001	1000 0	15 43
0 0003	3333 3	20 78
0 00016	6250 0	25 60
0 0001	10000 0	28 06

TABLE IV —SILVER NITRATE IN ANILINE.		
m	V	$\Lambda_m°$
0 1	10 0	0 666
0 01	100 0	0 327
0 003	333 3	0 436
0 001	1000 0	0 678
0 0003	3333 3	1 082
0 0001	10000 0	1 651

[1] Am Chem. J , 45, 295 (1911)

TABLE V.—SILVER NITRATE IN PYRIDINE.

m.	V.	Λ$_m$°.
0.1	10.0	24.80
0.01	100.0	33.85
0 003	333.3	43 68
0.001	1000 0	54.13
0.0003	3333 3	66.14
0.0001	10000.0	73 50
0.00006	16666 7	75 82

In Fig. 1 are plotted the values given in Tables I–IV. As a comparison, the results of other investigators are also given. The scale used in Fig. 1 being too small to show well the changes of conductance with dilution in solutions of silver nitrate in aniline, the results of Table V are plotted in Fig. 2 and compared with the results obtained by Sachanov[1] in more concentrated solutions. Curves similar to this conductance curve have
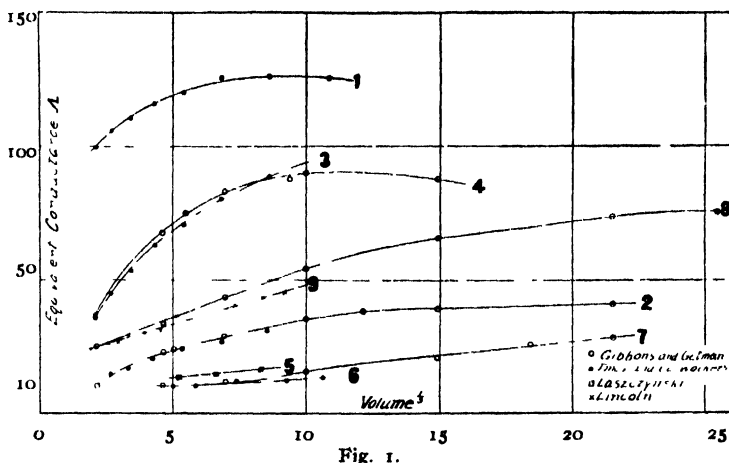
Fig. 1.

1, Conductance in Water   2, Conductance in Ethyl Alcohol   3 and 4, Conductance in Methyl Alcohol   5, Conductance in Acetone at 18°   6 and 7, Conductance in Acetone at 25°.   8 and 9, Conductance in Pyridine

been described by Franklin and Gibbs[2] for silver nitrate in solutions in methylamine, and by Shinn[3] for solutions of silver nitrate in ethylamine.

The conductance curve for silver nitrate in acetone at 18°, described by St. V. Laszizynski,[4] is also plotted in Fig. 1. As it lies above the curve obtained at 25° it indicates that the silver nitrate solutions in acetone have a negative temperature-coefficient. This phenomenon was observed

[1] Z. physik. Chem., 83, 129 (1913).
[2] THIS JOURNAL, 29, 1389 (1907)
[3] J. Phys. Chem., 11, 537 (1907).
[4] Z. Elektrochem., 2, 55 (1895).
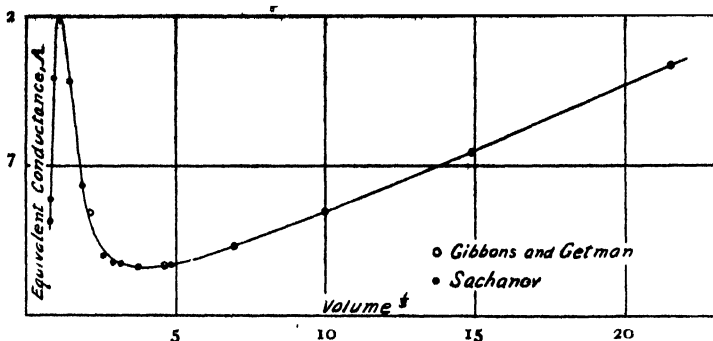
Fig. 2.—Conductance in Aniline.

by Cattaneo[1] for solutions of hydrochloric acid in ether, and by Getman and Gibbons[2] for solutions of zinc chloride in methyl alcohol.

3. Transport Numbers.

Since the data at hand, concerning the transport numbers of the ions of silver nitrate in nonaqueous solutions, were somewhat meager, it seemed best to carry out as full a series of such measurements as possible for the solutions under investigation.

Two forms of apparatus were employed for these determinations—the form designed by Mather and modified by Jones and Basset,[3] and a modified form of the Nernst-Loeb apparatus which has been designed in this laboratory and is illustrated in Fig. 3. The electrodes were in both cases made of pure silver wire fused to a stout piece of platinum wire which was in turn sealed into the glass tube and protected with fusion glass.
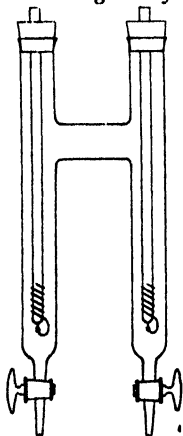
A copper coulometer was used to measure the total current Two copper plates, 2.2 by 5 cm. in dimensions, served as electrodes, one of which, the cathode, could be removed for cleaning and weighing. The solution in the coulometer was made up as follows: $CuSO_4.5H_2O$, 150 g.; H_2SO_4, 50 g.; C_2H_5OH, 50 g.; H_2O, 1000 g. During the passage of the current, a slow stream of carbon dioxide bubbled through the solution between the electrodes in the coulometer. The

Fig. 3.   laboratory electrical circuit served as a source of current and it remained fairly constant during the time of each experiment.

The Jones and Bassett cell was carefully calibrated. To simplify the

[1] *Atti accad. Lincei*, [5] 2, 295.
[2] *Am. Chem. J.*, 48, 124 (1912).
[3] *Ibid.*, 32, 429 (1904).

method given by them, the apparatus was leveled and filled with distilled water to a suitable height.   After marking each arm of the apparatus to indicate this level, it was emptied and thoroughly dried.   The stopcock was closed and each arm filled with distilled water from a carefully calibrated buret.   The volume required to fill each arm to the mark was noted.   The stopcock was then opened and water added until it again stood at the same level.   This operation was repeated three times with the following results:

I. Cc	II Cc	III. Cc.
55 56	55 83	112 21
55 54	55.80	112 23
55 45	55 76	112 24
55 45		

Average,	55 50	55 80	112 23

For each experiment 112.23 cc. of the solution were run into the apparatus from the buret and after inserting the electrodes it was placed in the thermostat.   When sufficient time had elapsed for the temperature to become uniform, it was connected in series with the coulometer, a variable resistance and a milliammeter.   The circuit was closed and the current allowed to pass through the solution several hours.   When a sufficient amount of silver had separated at the cathode, the stopcock was closed, the cell was removed from the thermostat and the two solutions were filtered through glass wool into two 100 cc flasks   Each arm was thoroughly rinsed several times and the wash water was added to the corresponding solution   After the solutions had acquired the temperature 'of the room they were diluted to 100 cc. and analyzed by Volhard's method. The ammonium thiocyanate solutions used were 0.1 and 0.025 N and were standardized against a corresponding aqueous solution of silver nitrate. The amount of silver in the solution was compared with the amount originally present.

This method was used for the measurement of the transport numbers of most of the solutions in methyl and ethyl alcohols.   The analysis of the solution from the cathode chamber seldom gave the same value for the transport number as the analysis of the solution from the anode chamber.   If any silver peroxide formed on the anode, the amount was very slight and the silver separated out in beautiful, shiny needles on the cathode.   By taking the mean of the two values so obtained, the agreement of results was fairly good.

It seemed probable that the cause of the irregularity observed was that the unaltered portion of the solution did not lie midway between the electrodes.   This would seem logical when the ions do not share equally in

carrying the current. Schlundt[1] found that in the case of solutions of silver nitrate in pyridine and acetonitrile the unaltered portion or "middle layer" was much nearer the anode than the cathode.

This experience led to the designing of the form of apparatus illustrated in Fig. 3. It was used in a few of the experiments with solutions in the alcohols and with the solutions in pyridine. The apparatus was filled to a level above the horizontal connecting tube and the electrodes were inserted. The stoppers carrying the electrodes had a slight groove cut on one side to allow for the expansion of the contents of the cell, but in no case did the solution come in contact with these rubber stoppers The outlet tubes of the two arms were protected by means of rubber caps sealed with glass rods. The apparatus was then placed in the thermostat and, after uniform temperature was acquired, connection with the circuit was made as in the previous experiments.

When sufficient silver had separated on the cathode, the following method was adopted to ascertain the exact position of the "middle layer." The solution was drawn from the anode arm into three or four tared glass stoppered weighing bottles, and the entire solution from the cathode arm was transferred to another weighing bottle. These portions were weighed and their content of silver determined by Volhard's method. These values were then compared with the amount of silver which would have been present if the solutions had maintained their original concentration. If there was a gain in silver, that portion was considered a part of the solution around the anode; if there was a loss in silver, that portion was considered a part of the solution around the cathode. If the change in the amount of silver present was less than 1%, that portion was considered the "middle layer." However, the amount of gain was added to the value for the solution around the anode or the amount of loss was added to the value for the solution around the cathode.

As an example, let us consider the measurements made with the 0.05 N solution of silver nitrate in ethyl alcohol.

	Wt of solution.	Orig wt of silver	Final wt of silver	Change in silver
I	9 2174	0 06206	0 10147	+0 03941
II	3 37880	0 02567	0 02533	+0 00034
III	3 0431	0 02063	0 02045	+0 00018
IV	9 1731	0 06229	0 05254	—0 00975
V	19 8476	0 13486	0 10598	—0 02888

Total solution in anode chamber   16.048 g

Transport number of anion .   0 613

Total solution in cathode chamber   29 021 g

Transport number of anion   .   0 593

Mean,   0 603

[1] *J Phys Chem*, 6, 159 (1902)

In this case, it is quite evident that if the division had been made exactly in the middle of the solution, accurate values could not have been obtained.

Tables VI to VIII give the results of the values obtained for the various solutions

m = concentration of the solutions (made up accurately by weight).

t = duration of the experiment in hours.

E = reading of the milliammeter in milliamperes.

A = the transport number of the anion (calculated from the analysis of the solution around the anode)

C = the transport number of the anion (calculated from the analysis of the solution around the cathode)

TABLE VI —SOLUTIONS IN ETHYL ALCOHOL

Apparatus	m	t	L	A	C	Mean	Mean of series
Jones and Bassett's	0 1	4	3 4	0 626	0 707	0 667	
	0 1	5	3–4	0 668	0 683	0 675	0 673
	0 1	5	3–4	0 632	0 718	0 676	
Jones and Bassett's	0 05	8	2 5–3	0 751	0 752	0 7515	
	0 05	10	2 5–3	0 697	0 729	0 713	0 733
	0 05	9	2 5–3	0 724	0 744	0 734	
Gibbons	0 05	4²/₃	4	0 613	0 593	0 603	0 603
Jones and Bassett's	0 04	10	2 5–3	0 728	0 693	0 710	
	0 04	10	2 5–3	0 705	0 717	0 711	0 7105

TABLE VII —SOLUTIONS IN METHYL ALCOHOL

Apparatus	m	t	Γ	A	C	Mean	Mean of series
Gibbons'	0 1	3	4–5	0 587	0 570	0 5785	
	0 1	3	4–5	0 584	0 572	0 578	0 578
Jones and Bassett's	0 1	3 5	5–8	0 765	0 571	0 668	0 617
Jones and Bassett's	0 07	3	5	0 637	0 607	0 617	
	0 07	3	5	0 767	0 600	0 684	0 650
Gibbons'	0 07	4	4–5	0 5805	0 568	0 574	0 574
Jones and Bassett's	0 05	3	5–6	0 561	0 604	0 5825	
	0 05	3 5	5–6	0 572	0 587	0 5795	0 581
Jones and Bassett's	0 04	3	5–6	0 560	0 572	0 566	
	0 04	4	5 5	0 616	0 622	0 619	
	0 04	4	5 5	0 576	0 572	0 574	0 579
	0 04	4	5 5	0 573	0 541	0 557	

TABLE VIII —SOLUTIONS IN PYRIDINE

Apparatus	m	t	E	A	C	Mean	Mean of series
Gibbons'	0 1	4	4–6	0 675	0 677	0 676	
	0 1	4	4–6	0 699	0 701	0 700	0 694
	0 1	4	4–6	0 698	0 717	0 707	
Gibbons'	0.05	5	3–5	0 667	0 691	0 679	
	0 05	4	3–5	0 656	0 697	0 676	0 677

Discussion of Above Tables.

Ethyl Alcohol.—Since the differences in the values obtained when Jones and Bassett's apparatus was used were so great, only the value obtained when Getman and Gibbons' apparatus was used will be compared with the values obtained by other investigators.

Methyl Alcohol.—The values for 0.1 and 0.07 N solutions obtained with Jones and Bassett's apparatus are considered much less accurate than the other values given in the above tables.

Acetone.—Attempts were made to determine experimentally the transport numbers in acetone solutions, but the maximum concentration that could be obtained even by shaking silver nitrate with acetone for 24 hrs. was only 0.01 N and the resistance of this solution was so great that the measurements were not considered trustworthy. This was the conclusion arrived at by Jones and Rouiller[1] in their work. Roshdestwensky and Lewis, from their electromotive force measurements of concentration cells, calculated the transport number for the anion of silver nitrate in acetone as 0.60 to 0.58 for dilutions ranging between 0.02 and 0.007 N. Jones and Rouiller determined the transport numbers for silver nitrate in mixtures of acetone and water. By extrapolation from the curves obtained by plotting their results, it seems probable that the value for a 0.01 N solution in pure acetone might lie between 0.60 and 0.62.

Pyridine.—The pyridine solutions could not be analyzed in the same way as an aqueous or an alcoholic solution, because of the basic and solvent properties of the pyridine. Two methods of eliminating the pyridine were tried: (1) the pyridine was neutralized with concentrated nitric acid; or (2) the greater part of the pyridine was distilled off from the solution before neutralizing it. The mixture of silver and pyridine nitrates was diluted with water and titrated with ammonium thiocyanate solution. The first method was less troublesome and gave fully as satisfactory results.

Aniline.—The analysis of the aniline solutions proved to be an insurmountable obstacle to the determination of the transport numbers in that solvent. All known methods were found to be impracticable.

Comparison of the Values as Given by Various Investigators.

TABLE IX.—SOLUTIONS IN ETHYL ALCOHOL.

$t°$.	m.	A.	Investigator.
20	0.108	0.594	Mather
25	0.076–0 101	0.5988	Jones and Bassett
25	0.02	0 616	Rouiller
25	0.05	0.603	Gibbons

[1] *Am. Chem. J.*, **36,** 475 (1906).

TABLE X.—SOLUTIONS IN METHYL ALCOHOL.

$t°$	m	4	Investigator
?	?	0 533	Campetti
25	0 0093	0 523	Carrara
25	0 10	0 5797	Jones and Bassett
25	0 02	0 572	Jones and Rouiller
25	0 10	0 578	Gibbons
25	0 07	0 574	Gibbons
25	0 05	0 581	Gibbons
25	0 04	0 570	Gibbons
21	0 1	0 613	Schlundt
22	0 025	0 564	Schlundt
22	0 025	0 554	Schlundt
25	0 1	0 694	Gibbons
25	0 05	0 677	Gibbons

4. Electromotive Force.

The electromotive force of cells of the following types was studied

(1) Ag | AgNO$_3$, Conc. I | AgNO$_3$, Conc. II | Ag,

the solvent in the two solutions being identical, and

(2) Ag | AgNO$_3$, Aqueous | AgNO$_3$, Nonaqueous | Ag,

the solvents being different but the concentrations being identical. The more concentrated solutions were all made up at room temperature by direct weighing. The dilutions were made from these by means of carefully calibrated burets and flasks. The solutions were kept in the dark, and in no case was there more than a very slight tendency to turn brown, even when left standing several weeks.

The compensation method of Poggendorff was employed, an enclosed type of Lippmann electrometer being used as a zero instrument. Measurements with this instrument were correct to one millivolt, except when the poor conductance of the solutions or other disturbing factors introduced a larger error. The experimental cell was balanced against a chloride accumulator as a source of potential. The electromotive force of this cell was determined by means of a certified Weston Standard Element, before and after each measurement of the experimental cell. The electromotive force of this Standard Element was 1.01948 volts at 25°.

The experimental cell, illustrated in Fig. 4, consisted of two parts connected by means of a tight-fitting piece of rubber tubing. During an experiment, the stopcock S, of fairly large bore, was kept closed,
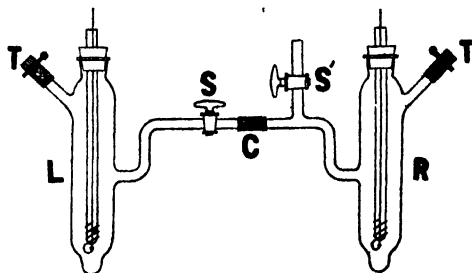
Fig. 4.

except while the measurements were actually being made. The electrodes were made of pure silver wire sealed to a stout piece of platinum wire, which, in turn, was sealed into a glass supporting tube and protected by fusion glass. The electrical connections were made through mercury placed in these glass tubes.

At first, some difficulty was experienced in obtaining constant values for the electromotive force of a given concentration cell, but by adopting the following method of procedure the electromotive force remained constant for at least 30 min after contact between the two solutions had been made   The two half-cells were connected together at C and with the two stopcocks S and S' closed, the two solutions were poured into the cell until they were at the same level on each side, the denser solution being always put into the half-cell R. When the electrodes had been inserted and the clamps T and T' closed, the cell was supported in the thermostat and allowed to stand 25–30 min. in order to acquire a uniform temperature. Connection with the circuit was then established and the contact between the two solutions made as follows. The stopcock S' and clamp T' were opened and, by gently blowing into a pipet inserted at T', the denser solution in R was forced up to the base of the tube carrying the stopcock S'. The clamp T' was then closed and the stopcock S and clamp T were opened   By blowing very gently into a pipet inserted at T, the solution in L was brought into contact with the first solution   The stopcocks S and S' and the clamp T were then closed.   A measurement of the electromotive force was made at once.   The stopcock S was opened just long enough to determine the point of balance on the bridge wire.

TABLE XII

m_1	m_2	E	K	m_1	m_2	E	K
	Solutions in Ethyl Alcohol				Solutions in Acetone		
0 1	0 01	0 0408	0 0591	0 01	0 003	0 0293	0 0601
0 1	0 003	0 0650	0 0587	0 01	0 001	0 0537	0 0630
0 1	0 001	0 0922	0 0619	0 01	0 0003	0 0816	0 0665
0 1	0 0003	0 1297	0 0658	0 01	0 0001	0 1212	0 0771
0 1	0 0001	0 1648	0 0680		Solutions in Aniline.		
0 01	0 003	0 0276	0 0640	0 1	0 01	0 0373	0 0285
0 01	0 001	0 0538	0 0657	0 1	0 003	0 0548	0 0321
0 01	0 0003	0 0858	0 0670		Solutions in Pyridine		
0 01	0 0001	0 1169	0 0674	0 1	0 01	0 0368	0 0425
	Solutions in Methyl Alcohol			0 1	0 003	0 0592	0 0460
0 1	0 01	0 0462	0 0636	0 1	0 001	0 0831	0 0500
0 1	0 003	0 0746	0 0639	0 1	0 0003	0 1105	0 0577
0 1	0 001	0 1008	0 0626	0 1	0 0001	0 1375	0 0544
0 1	0 0003	0 1358	0 0634	0 1	0 00006	0 1532	0 0560
0 1	0 0001	0 1719	0 0637	0 01	0 003	0 0207	0 0502
0 01	0 003	0 0264	0 0600	0 01	0 001	0 0437	0 0549
0 01	0 001	0 0591	0 0670	0 01	0 0003	0 0723	0 0587
0 01	0 0003	0 0934	0 0675	0 01	0 0001	0 0978	0 0588
0 01	0 0001	0 1337	0 0677	0 01	0.00006	0 1179	0.0630

Two other readings were made at intervals of ten minutes The electromotive forces calculated from these three bridge readings seldom varied from the mean value by more than one- or two tenths of a millivolt

The results of the measurements are given in Table XII The constant K was calculated from the Nernst formula, written in the following form The value of the transport number was assumed not to vary appreciably with the concentration

$$K = -\frac{E}{\log_{10} m_1\Lambda_1/m_2\Lambda_2} \quad (5)$$

When it was assumed that the observed values of the transport numbers were correct, and that they did not vary appreciably with the dilution the values for E calculated for the different cells showed, in no case, very close agreement with those observed

In Table XIII the calculated and observed values for the transport number (n) of the anion of silver nitrate in the various solvents are given (n) is calculated from the formula

$$n = \frac{v}{u + v} = \frac{E}{2 \times 0\ 0595 \log_{10}(m_2\Lambda_1/m_2\Lambda_2)} \quad (6)$$

and the observed value is in each case the mean of the value given in Tables IX XI, excluding those found by Campetti and Carrara

TABLE XIII

m	m	n Calc	n Obs	m_1	m_2	n Calc	n Obs
Solutions in Ethyl Alcohol				Solutions in Acetone			
0 1	0 01	0 496	0 603	0 01	0 003	0 505	0 62[1]
0 1	0 003	0 493		0 01	0 001	0 541	
0 1	0 001	0 520		0 01	0 0003	0 559	
0 1	0 0003	0 553		0 01	0 0001	0 647	
0 1	0 0001	0 571		Solutions in Aniline			
0 01	0 003	0 557		0 1	0 01	0 239	
0 01	0 001	0 565		0 1	0 003	0 490	
0 01	0 0003	0 567		Solutions in Pyridine			
0 01	0 0001	0 566		0	0 01	0 357	0 620
Solutions in Methyl Alcohol				0	0 003	0 390	
0 1	0 01	0 534	0 577	0	0 001	0 420	
0 1	0 003	0 537		0	0 0003	0 443	
0 1	0 001	0 526		0	0 0001	0 457	
0 1	0 0003	0 533		0	0 00006	0 471	
0 1	0 0001	0 535		0 01	0 003	0 422	
0 01	0 003	0 504		0 01	0 001	0 461	
0 01	0 001	0 563		0 01	0 0003	0 493	
0 01	0 0003	0 554		0 01	0 0001	0 494	
0 01	0 0001	0 569		0 01	0 00006	0 529	

The electromotive forces of the combinations

Ag | 0.1 N AgNO$_3$ in water | 0 1 N AgNO$_3$ in solvent II | Ag

[1] This value is extrapolated

were measured and the results are tabulated below. The first column designates the nature of the solvent II, E the observed potential, E_1 the electrode potential in the aqueous solution, E_2 the potential at the junction between the two liquids which is calculated according to Cumming's formula given on page 1636, and E_3 is the electrode potential in solution II. The electrode potentials are referred to that of the hydrogen electrode as zero.. The electrode potential E_1 in aqueous solution is calculated by means of the formula $E = E_p - 0.0595 \log m$, in which the value of E_p is taken as 0.798 volt

TABLE XIV.

Solvent II	L.	E_1	E_2	E_3
Ethyl alcohol.	+0 1004	+0 7331	+0 00217	+0 8314
Methyl alcohol.	+0 0967	+0 7331	—0 00005	+0 8298
Acetone	+0 1712	+0 7331	+0 00202	+0 9022
Aniline	—0 2559	+0 7331		
Pyridine.	—0 3618	+0 7331	—0 00017	+0 3711

5. Discussion of Results.

An inspection of Figs. 1 and 2 brings to light certain differences between the conductance curves for nonaqueous solutions and the curve for aqueous solutions of silver nitrate. Considering the latter to represent a normal curve of conductance, the curves for nonaqueous solutions present certain abnormalities. This abnormality is most clearly shown in the curve for solutions in aniline and less clearly in the curves for solutions in acetone and pyridine. The curve for solutions in ethyl alcohol is quite similar to that for solutions in water, except that in the more concentrated region it appears somewhat flatter; while the curve for solutions in methyl alcohol shows a tendency to pass through a maximum in the more dilute regions

In seeking a cause for these abnormalities it is important to consider the determination of the molecular weight of silver nitrate in these solvents. In certain cases, at the temperature of the boiling solvent, there is considerable interaction between the solvent and the salt, which renders the determination of the molecular weight extremely difficult This is especially true when aniline is the solvent and true to a lesser degree in the other solvents. It is, however, a well known fact that these liquids show a great tendency to combine with the ions and that there are also present in such solutions polymerized molecules of the dissolved salt. Jones[1] showed that sodium iodide, cadmium iodide, and ammonium thiocyanate were polymerized to an appreciable extent when in solution in acetone. It has been shown by many investigators that in solutions in ethyl and methyl alcohol the solute frequently exists in a polymeric state.

[1] *Am. Chem. J*, **27**, 16 (1902).

Getman and Gibbons[1] have shown this to be the case for zinc chloride. The molecular weight of silver nitrate in pyridine, as determined by Werner-Smujlow,[2] is 165.42 (mean value of series ranging from 160.02–169.82) but, as determined by Speransky and Goldberg,[3] it is 207.5 (mean value of series ranging from 199–210). This latter result was confirmed by Schroeder[4] who found the molecular weight to be 203.6 (mean value of series ranging from 186- 214). By studying the equilibrium of the system, silver nitrate in pyridine from $-65°$ to $+110°$, Kahlenberg and Brewer[5] discovered that these substances combine to form definite compounds at different temperatures and that, between $-24°$ and $+48.5°$, the solid phase had the composition $AgNO_3.3C_5H_5N$, while above $79°$ there was no combination of the two substances, pure silver nitrate being in equilibrium with the solvent. This shows clearly that the molecular complexity of the solute at $25°$ would be even greater than at $115°$, the boiling point of pyridine.

That there is a possibility of three different reactions taking place in solution where such complexes exist was discussed by Sachanov.[6] The complexes C_m may decompose into simpler molecules, or they may ionize to form complex ions, or the simple molecules may ionize to form simple ions. These reactions can be represented as follows:

$$C_m \rightleftarrows mC,$$
$$C_m \rightleftarrows A' + K',$$
$$C \rightleftarrows A + K,$$
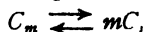
where A' and K' denote the complex anion and cation, and A and K denote the simple anion and cation. The first two equations would hold true whether the complex was a polymerized molecule of the solute or a compound of solute and solvent. Walden[7] considers that ionization is caused and induced by the process of disaggregation of the polymerized salt molecules. In case the solvent has a high dielectric constant, this depolymerization into simple ions will be abrupt, and in a solvent with a low dielectric constant this change will be more gradual or the effect of the complexes will be more marked and prolonged. Arranging these solvents in the order of their dielectric constants, we see that the degree of the abnormality of the conductance curves follows practically the same order. This is shown in the following tabulation:

[1] *Am. Chem. J.*, **48**, 124 (1912).
[2] *Z. anorg. Chem.*, **15**, 18 (1897).
[3] *Z. physik. Chem.*, **39**, 369 (1902).
[4] *Z. anorg. Chem.*, **44**, 20 (1905).
[5] *J. Phys. Chem.*, **12**, 283 (1908).
[6] *Z. physik. Chem.*, **83**, 129 (1913).
[7] THIS JOURNAL, **35**, 1649 (1913).

Solvent	D C
Water .	81.1
Methyl alcohol	31.2
Ethyl alcohol .	25 8
Acetone .	21 5
Pyridine	12 4
Aniline . .	6 85

Sachanov and Prscheborowsky[1] investigated the conductance of various electrolytes in six different solvents of very small dielectric constants. Many electrolytes showed maxima in very concentrated solutions, but in no case was a minimum observed They concluded that this might be due to the very small dielectric constant of the solvent.

The diminution in conductance with increasing molar concentration, as shown by extremely concentrated solutions of silver nitrate in aniline, has been ascribed by Kraus[2] to the influence of the increasing viscosity of the solutions. Sachanov has shown[3] that, if the equivalent conductance Λ is multiplied by the ratio of the viscosity of the solution to that of the solvent, η'/η, values are obtained which correspond to Λ for solutions where the two viscosities are approximately equal.

As the temperature is increased the abnormalities in a conductance curve diminish   Jones and his co-workers[4] clearly stated the relations between the temperature and the conductance of an electrolyte in an aqueous solution. They showed that (1) the temperature coefficient of conductance of aqueous solutions of electrolytes is greater the greater the hydrating power of the electrolyte, that (2) the temperature coefficients of conductance for any given electrolyte increase with the dilution of the solution and this increase is greatest for those substances with large hydrating power. These two statements led to the conclusion that the decreasing complexity of the hydrates with rise of temperature is a very important factor in conditioning the large temperature coefficients of conductance shown by those substances which have a large hydrating power. It would seem that the abnormalities observed in nonaqueous solutions might also be explained in a similar way.

The values of the transport numbers calculated from the electromotive force measurements of concentration cells are quite different from those obtained experimentally. In all cases the experimental values are the larger. The direct measurement could only be carried out with solutions of fairly large concentrations (not less than 0.02 N). It can be seen that the values calculated for the extremely dilute solutions approach more nearly the experimental values. The transport numbers, in all the sol-

[1] *Z Elektrochem* , **20,** 39 (1914)

[2] This Journal, **36,** 60 (1914)

[3] *Z physik Chem* , **83,** 129 (1913).

[4] "Hydrates in Aqueous Solution," *Publ Carnegie Inst* , **60,** pp. 156–7 (1907).

vents for which experimental or calculated data could be obtained, show an increase in the value for the anion with increasing dilution, with the exception of the experimental values for solution in pyridine where the opposite effect is apparent   The values for solutions in methyl alcohol show a much greater degree of uniformity for calculated and observed values as well as much better agreement between the two series   In the determination of the transport numbers it was observed that the "middle layer" did not lie midway between the electrodes   If one examines the experimental data of Schlundt[1] for a solution of silver nitrate in pyridine, one notices this same fact   He found a ' middle layer" less than one third the distance from the anode   The middle layer for the alcoholic solutions was situated much nearer the median line of the cell   It has been proved by Kahlenberg and Brewer[2] that pyridine and silver nitrate combine at ordinary temperatures to form complex molecules, and Mor gan and Kanolt[3] found that in a mixture of water and pyridine a large proportion of the pyridine traveled with the silver ions to the cathode LeBlanc, in his   Textbook of Electrochemistry" (page 76), calls atten tion to Kohlrausch's discovery that, with monatomic univalent ions, the transport numbers of all solutes in aqueous solutions approach the value 0 50 with increasing temperature   He states that at the same time the difference in mobility of the two ions in each case actually increases

The greatest shifting of the 'middle layer" was observed when pyridine was used as the solvent for the silver nitrate and definite compounds of solvent and solute are known to exist in such solutions   If the cation carries with it a part of the solvent, the concentration of the silver in the cathode chamber will be abnormally low and a corresponding increase will be observed in the anode chamber   It seems probable that the move ment of the solvent with the cation causes the shifting of the "middle layer" toward the anode   If the solvent moves with the anion, the "middle layer" should then shift toward the cathode   These ionic complexes break down more or less completely with increasing temperature and cause the transport numbers to approach a limiting value in aqueous solutions Probably, when sufficient experimental data has been' accumulated, it will be found that the transport numbers in nonaqueous solutions approach similar limiting values.

If the transport numbers do not increase with the dilution of the solu tion, K as calculated in Table XII should have a constant value, but it is only in the case of solutions in methyl alcohol that K has an even ap proximate constancy.   In the four other solvents, K increases steadily in value with the increasing difference in the concentration of the solutions

[1] *J Phys Chem*, **6,** 159 (1902)

[2] *Ibid.*, **12, 283** (1908)

[3] *Z physik Chem*, **48,** 365 (1904), THIS JOURNAL, **28,** 572 (1906)

in the cell. Likewise, the values of the transport numbers calculated in Table XIII, show a steady increase with the changing difference of concentration in the cell. Both of these phenomena may be due to the same cause. The degree of the dissociation of the conducting complexes into simple ions will increase as the solution is diluted. In the more concentrated solutions the molar concentration is not correctly given by the weight of silver nitrate in a given volume of solution, hence $m\Lambda$ is the true value of the ionic concentration only in dilute solutions. The change in value of this factor would cause an increase in the computed value for both n and K (as is shown by Equations (5) and (6)). The fact that this abnormality is greatest in the case of aniline and pyridine, where the effect of the complexes is most clearly shown in the conductance curve, seems to substantiate this view. The Nernst equation, therefore, is not a true expression of all the factors which determine the difference of potential in these concentration cells.

In comparing the electromotive forces found when an aqueous solution was joined to a nonaqueous solution of the same concentration, it is at once noticed that, whereas the solutions in the alcohols and acetone are positive toward the aqueous solution, the solutions in aniline and pyridine are negative toward the aqueous solution. The value obtained by Isgarischew[1] for the electrode potential of silver in solutions of silver nitrate in methyl alcohol is slightly greater than the one given in Table XIV; but he used the Henderson formula for calculating the potential at the junction of the two liquids and this involved the use of Λ_∞ which is by no means surely established. The value here given, therefore, seems more probable, since only experimental data were used in this calculation.

6. Summary.

The results obtained may be summarized as follows:

1. Conductance measurements of solutions of silver nitrate in ethyl alcohol, methyl alcohol, acetone, aniline and pyridine have been made for concentrations ranging between 0.1 and 0.0001 N. It has been shown that the conductance curve for solutions in aniline approaches a second maximum as the solutions become more dilute. It has also been shown that there is a relationship between the dielectric constant and the abnormalities of all the conductance curves.

2. The transport numbers of silver nitrate in ethyl alcohol, methyl alcohol and pyridine have been determined experimentally.

3. Measurements of the electromotive force have been made for a large number of concentration cells in the various solvents, an apparatus being used which is free from defects due to capillarity and constant communication of the two liquids.

[1] Z. Elektrochem., 19, 491 (1913).

4. Values for the electrode potential of silver in the various solvents have been calculated.

5. The experimental data seem to prove that the abnormalities observed in nonaqueous solutions of silver nitrate are due to the combination of the solvent and the solute to form complex compounds which dissociate more or less gradually.

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1914   "Verbindung des gelösten Körpers und des Losungsmittels in der Lösung ' Dhar, *Z Elektrochem* , **20,** 57

Ionic Velocities.

1888   "Ueberfuhrungszahlen und Leitvermögen einiger Silbersalze,' Loeb and Nernst *Z physik Chem* , **2,** 948

1894   "Der Einfluss der Losungsmittel auf die Beweglichkeit der Ionen," Campetti, *Nuovo Cimento*, [3] **35,** 225

1901   "A New Apparatus for Determining the Relative Velocity of Ions, with Some Results for Silver Ions," Mather, *Am Chem J* **26,** 473

1902   "On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile,' Schlundt, *J Phys Chem* **6,** 159

1904   "Determination of the Relative Velocities of Ions of Silver Nitrate in Mixtures of Alcohol and Water,   Jones and Bassett *Am Chem J* **32,** 409

1904   ' Uber die Verbindung der Lösungsmittel mit den Ionen ' Morgan und Kanolt, *Z physik Chem* , **48,** 365

1906   "The Compounds of a Solvent with the Ions " Morgan and ' nolt, *J Chem Soc* , **28,** 572

1906   "The Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone together with the Conductivity of Such Solutions,' Jones and Rouiller, *Am Chem J* , **36,** 427

1912 · "Calculation of Ionic Velocities of Silver Nitrate in Acetone Solutions " Roshdestwensky and Lewis, *J Chem Soc* , **101,** 2097

Molecular Weight.

1897   "Molekulargewichtsbestimmungen in Pyridin," Werner und Schmujlow, *J anorg Chem* , **15,** 18

1902   "The Molecular Weights of Certain Salts in Acetone, H C Jones *Am Chem J* , **27,** 16

1902   "Elektrolyse einiger anorganischen Salze in organischen Losungsmitteln, ' Speransky und Goldberg, *Z physik Chem* , **39,** 369

1905   "Verhalten von Silbersalzen in Pyridin," Schroeder, *Z anorg Chem* , **44,** 20

1908   "Equilibrium in the System Silver Nitrate and Pyridine   Kahlenberg and Brewer, *J Phys Chem* , **12,** 283

A THEORY OF VALENCY AND MOLECULAR STRUCTURE.

BY WILLIAM C ARSEM
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Introduction   Historical   Outline of Theory   (*a*) Structure of Molecules, (*b*) Multiple Valency, (*c*) Valency Relations in the Periodic System   Applications of the Theory   (*a*) Mechanism of Reactions, (*b*) Tautomerism, (*c*) Conduction in Metals, (*d*) Association, (*e*) Dissociation and Conduction in Electrolytes, (*f*) Dissociation and Conduction in Gases, (*g*) The Charge and Apparent Mass of an Electron

Introduction.

The purpose of this paper is to advance a theory of molecular structure

and valency and to attempt to explain certain phenomena by means of it.

The main features of the theory were conceived about ten years ago, and have been in process of development and extension since that time. Recently, however, some papers have appeared which contain ideas somewhat similar to my own. Among these was a paper by Sir William Ramsay,[1] in which he advanced the view that an electron may serve as a bond between the atoms in a compound, and that the electron behaves like an atom of an element. On this basis he gave explanations of certain chemical and electrochemical phenomena.

Practically the same idea has been used by P. Achalme,[2] to explain the formation of neutral molecules at the electrodes during electrolysis, and to show the mechanism of one type of gaseous ionization.

I have, therefore, ventured to present my views at this time with a feeling that they are in harmony with the present trend of scientific speculation.

Any theory of the nature of valency, or of the forces which hold atoms together in a molecule, should explain a number of facts, such as are here briefly summarized:

1. The combination of a "positive element" and a "negative element," to produce a stable compound.

2. The union of two atoms of a "positive" element, such as hydrogen, with each other, or the combination of two atoms of a "negative element," such as chlorine, with each other.

3. The formation of double salts and salts with water of crystallization.

4. The existence of monatomic molecules.

5. The absence of chemical affinity in the gases of the helium group.

6. Ionization and conduction in gases.

7. The mechanism of chemical reactions.

8. The phenomena of electrolysis and dissociation.

Valency is ordinarily assumed to be a property of free atoms; that is, we say the hydrogen atom is univalent, or that the aluminium atom is trivalent; but it seems to me more logical to consider valency as a property of atoms in a state of combination, since we know very little about free atoms, except in the case of the monatomic gases.

For example, in considering the combination of hydrogen and chlorine, we should attempt to find an explanation, not for the *union* of *atoms* of hydrogen and chlorine, but for the existence and stability of the *molecules* of these elements, and for reactions which take place between the *molecules*. The meaning of this statement will become clearer after the explanation of the theory has been read.

[1] *Trans. Chem. Soc.*, 93, I, 774 (1908).
[2] *Compt. Rend.*, 134, 647 (1912).

Historical and Critical.

The history of the electron conception of valency really began with the attempts of Davy and of Berzelius to explain chemical affinity by assuming that electric charges were associated with the atoms. This theory required that the atom of a given element should possess a charge of the same sign in all its compounds, but when it was discovered that a great many compounds could be made, whose very existence would seem to be contrary to these views, the theory of Berzelius, in its original form, lost the enthusiastic support which it had received at first.

The development of the electron theory has recently led to a revival of the views of Berzelius in a modified form.   J. J. Thomson[1] has advanced the idea that an atom is a system of revolving electrons, of greater or less stability, capable of gaining or losing a certain number of electrons without sensibly changing its configuration.   He uses the terms "positive valency" and "negative valency," and explains positive valency as the ability of an atom to lose electrons, and negative valency as the power to gain electrons. He regards the combination between two atoms as involving a permanent transfer of one or more electrons from one atom to the other, the atom which gains electrons becoming negative, while the one which loses electrons becomes positive.   The direction of the electric force between two atoms in a compound will then depend upon the direction in which the transfer has taken place.   This assumption requires, as J. J. Thomson points out, that the bond should have direction.

Thomson's conception of valency as a vector phenomenon has been developed at considerable length by Falk and Nelson,[2] and by Fry[3] in connection with some organic compounds and reactions.

Thomson, and also Falk and Nelson, take some hypothetical free atoms, having no charges, then proceed to combine them and assume that an electron is permanently transferred.   This would seem to be an inverted method of constructing a theory.   We deal almost entirely with molecules, and know very little about free atoms, certainly not enough to postulate the existence of uncharged free atoms of elements like hydrogen and chlorine.   The idea that a bond is formed by the permanent transfer of an electron, involves numerous difficulties, one of which is that the separate atoms in a compound should be charged.   I know of no experimental evidence showing that portions of a saturated molecule are charged differently.   The fact that many substances can be dissociated into oppositely charged atoms or groups does not prove that these atoms or groups are permanently charged in the same way when in the undissociated compound.

[1] "Corpuscular Theory of Matter."

[2] *School of Mines Quarterly*, Columbia Univ., **33**, 179, 980; THIS JOURNAL, **32**, 1637 (1910).

[3] THIS JOURNAL, **36**, 248 and 262 (1914).

There is a difficulty in accounting, on the basis of Thomson's theory, for the existence of a hydrogen molecule made up of two positive atoms, or of a chlorine molecule with two negative atoms, and it is hard to see why two neutral atoms or two atoms having equal valency of the same sign should combine to form a stable molecule. In general, it seems as though binary elementary molecules should be incapable of existence on the basis of this theory.

Bray and Branch[1] find difficulties in the application of Falk and Nelson's conception of valency and introduce the ideas of polar and non-polar valency according to which an "electron passes completely or does not pass from one atom to the other."

Lewis[2] adopts their terms "valence number" and "polar number," the former a pure integer, the latter a positive or negative integer, and assumes three types of chemical compound; the polar type, in which the electrons occupy fixed positions within the atom; the non-polar type, in which the electrons move freely from atom to atom within the molecule; and the metallic type, in which the electron is free to move even outside the molecule. He criticizes the structural formulas of Falk and Nelson and of Bray and Branch, showing that, in certain cases such as

$$\text{H} \longrightarrow \text{O} \rightleftharpoons \text{O} \longleftarrow \text{H},$$
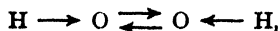
they either have no meaning or that the atoms are not bonded together where the arrows have opposite directions.

Some of the objections to Thomson's theory and Falk and Nelson's extension of it have been outlined in a recent article by Bates.[3]

Stark's theory[4] like Ramsay's, assumes that chemical combination between two atoms represents "a simultaneous attraction of both atoms for the same electron, which thus forms a bond between them." He supposes that a monovalent electropositive atom can be neutralized by a single valence-electron which is at an appreciable distance from the atom. The objection to this view is that it assumes that monovalent atoms in the free state may be neutral, whereas, to my knowledge, this has never been shown to be the case.

Outline of the Theory.

(a) *Structure of Molecules.*—Regarding molecules and atoms as systems of moving electrons, I shall treat valency as a consequence of the relative stability of these systems. An attempt will be made to apply the theory to explain certain phenomena, and to show that it is consistent with the observed facts.

Considering the simple case of a binary molecule in which the atoms are

[1] This Journal, 35, 1440 (1913).
[2] *Ibid.*, 1448 (1913).
[3] This Journal, 36, 789 (1914).
[4] Campbell's Modern Elect. Theory, 2nd. Ed., March, 1913.

monovalent, the theory supposes that the molecule is a stable system composed in turn of two systems or sub-groups of moving electrons which we call atoms, the dynamic equilibrium being such that one electron oscillates periodically from one system to the other, and is common to both systems, neither of which is complete in itself. This oscillating electron I shall call the valence-electron, since this term has come into use.

Although I speak of the valence-electron as oscillating, it might have any kind of motion such as revolution in an orbit or motion in a complex curvilinear path. It can be considered as forming a connecting link between the two atoms, being an integral part of each atom in turn. I have developed the theory as though each bond corresponded to a single valence-electron. It is, of course, conceivable that a group or system of electrons might perform the same function.

Valency is the property, or power, which an atom possesses of sharing a certain number of electrons with one or more other atoms, in such a way that the atoms so united form a *complete* or *perfect* electron system which is electrically neutral.

If a single valence-electron be assumed to be characteristic of a monovalent union, unit valency of an atom or radical in a compound may be defined as the power or property of sharing one oscillating electron with another atom or radical.

The hydrogen molecule, for example, can be represented as in Fig. 1, the black dot indicating the valence-electron, and the dotted line its path of oscillation. For convenience, the atoms in the molecule are represented as spheres in contact at a single point because, in the present state of our knowledge, this kind of a mental picture answers the purpose perhaps as well as any other. Very probably the method of union is much more intimate than such a diagram indicates. The separate atoms may even lose their identity when combined to form a molecule as suggested by A. A. Noyes.[1]

It is evident that the molecule cannot be *symmetrically* divided into two equivalent parts. If it is divided, one of the atoms will retain the valence-electron, and the other will be without it, and the two will become oppositely charged ions. (See Fig. 18.) In an ion therefore, unit valency corresponds to an excess or deficiency of half an electron.

A *free* hydrogen atom will, therefore, be either negative or positive, according as it does, or does not, retain the valence-electron, and its charge will be $1/2$ the charge of an electron, or $\epsilon/2$. (The symbol ϵ, used in this paper for the charge of an electron, is not to be confused with the charge of a univalent ion, which I have denoted by e. The relation between these quantities is discussed below.)

The hydrogen molecule can also be considered as two "partial atoms,"

[1] THIS JOURNAL, 30, 351-2 (1908).

or "incomplete systems," both positive, held together by a negative valence-electron, and thus forming a "complete" or perfect system. The
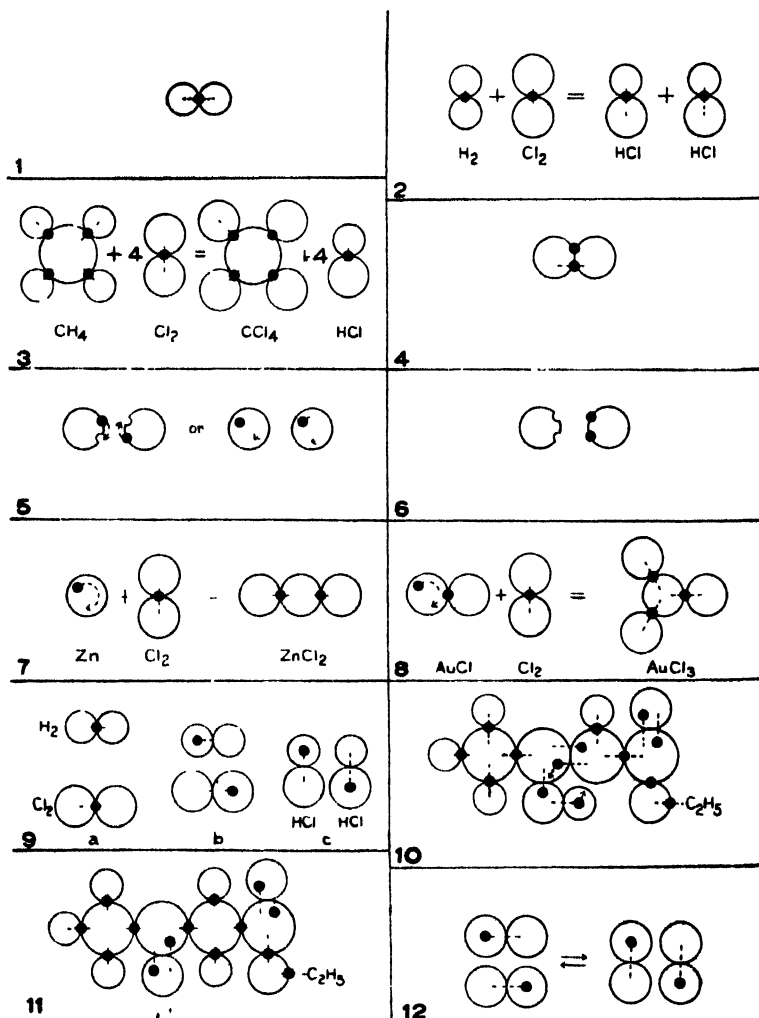
Fig. 1.—Hydrogen molecule.
Fig. 2.—Formation of hydrochloric acid.
Fig. 3.—Chlorination of methane.
Fig. 4.—Oxygen molecule.
Fig. 5.—Dissociated oxygen, not ionized.
Fig. 6.—Dissociated oxygen, ionized.

Fig. 7.—Formation of zinc chloride.
Fig. 8.—Formation of auric chloride.
Fig. 9.—Formation of hydrochloric acid.
Fig. 10.—Enol form of acetacetic ester.
Fig. 11.—Keto form of acetacetic ester.
Fig. 12.—"Free electrons" in metals.

structure of binary molecules of other monovalent elements, such as chlorine and bromine, should be exactly similar to that of hydrogen.

Fig 13.—Conduction in metals
Fig. 14.—Ionized hydrochloric acid
Fig. 15 —Polarized anode
Fig. 16.—Discharge of negative chlorine ions at anode, forming positive chlorine ions

Fig. 17 —Ionized zinc chloride
Fig 18 —Partial dissociation of hydrogen
Fig. 19 —Complete dissociation of hydrogen
Fig 20 —Ionization of helium

Such a view of the relation of the atom to the molecule avoids the necessity of differentiating the elements as positive or negative (An ion may be positive or negative, but an atom in a compound has no sign) Its advantages will be illustrated by a few examples.

A molecule of hydrochloric acid is composed of a "partial atom" of hydrogen and one of chlorine, held together by a valence-electron, and the synthesis of hydrochloric acid from hydrogen and chlorine may be repre sented as in Fig 2, the molecules of H_2, Cl_2 and HCl having similar struc tures

A molecule of carbon tetrachloride is composed of a "partial atom" of carbon and four "partial atoms" of chlorine, held together by four valence electrons The substitution of hydrogen in methane by chlorine to form carbon tetrachloride takes place as shown in Fig 3.

In this reaction, four "partial atoms" of chlorine exchange places with four "partial atoms" of hydrogen

If considered apart from the valence-electrons, all atoms (partial atoms) will be positive

A molecule of a divalent element, such as oxygen, containing two atoms, will have two valence-electrons, and may be represented as in Fig 4 Such a molecule differs from one in which the atoms are monovalent, for in this case the molecule *can* be divided so that each atom retains one of the valence-electrons

A molecule thus divided could be represented in either of two ways as in Fig 5

Each of these atoms is therefore electrically neutral, since it is at the same time positive by half an electron, and negative by half an electron We should expect, therefore, to find that some *divalent* elements are stable in the monatomic condition, and we know this to be the case with zinc, cadmium and mercury.

If we exclude dissociation phenomena, we may deduce from the theory the general principle that only the elements of even valency—that is, elements of groups 0, 2, 4, 6, and 8 of the periodic system—should be capable of forming stable monatomic molecules

A binary molecule of a divalent element will also have an alternative method of splitting, so that one of the atoms will have both of the valence-electrons (See Fig 6) In this case, each atom will have a double charge or $2 \times \epsilon/2$, one atom having the charge $+ \epsilon$ and the other the charge $- \epsilon$

Comparing the chief theories of valency with my own, it will be seen that Ramsay and Stark each assume that the valence-electron is attached in some way to both the atoms which it joins, but do not claim that it forms an integral part of each atom Moreover, Stark's valence-electron is at some distance from both the atoms which it joins, and does not enter

the atoms at all.   J. J. Thomson, Falk and Nelson, H. S. Fry, and others assume that the valence-electron is permanently transferred in one or the other direction across the point of union of two atoms.   My theory assumes that the valence-electron oscillates continually between the atoms which it joins and forms an integral part of each

(b) *Multiple Valency*.—The valency of each element was at one time assumed to be constant, and in cases where two elements combined in more than one proportion, some of the molecular formulas were doubled to make them agree with the theory.   This belief gradually lost ground, and it now appears to be generally admitted that most elements can exhibit multiple valency.   Moreover, there is much evidence in support of the belief that in such cases the several valencies of an element will differ successively by two.   This is in perfect agreement with the new theory, as will be shown

Multiple valency may be explained by an example as follows if we assume that a free zinc atom has zero valency, then when zinc combines with chlorine, one of the electrons of the zinc atom must become a valence-electron.   But since this electron must oscillate so that it is out of the atom half of the time, another electron must be supplied to maintain equilibrium.   This electron is supplied by the chlorine, the valence-electron which previously held the chlorine atoms together in the chlorine molecule now serving to unite the second atom of chlorine to the zinc.   The reaction is illustrated in Fig. 7.

The net result of these changes is that the valency of zinc is increased from zero to 2.   If another electron should become a valence-electron, the valency of the zinc atom would in the same way be increased to 4.   An increase of valency, when it is originally *odd*, can occur in like manner, for instance, in aurous chloride, if another electron in the gold atom becomes a valence-electron, the valency will be increased by two, as in the case of zinc, so that when aurous chloride takes up more chlorine, the trichloride is formed.   (See Fig. 8.)

The gold in aurous chloride can, therefore, be said to have a *latent valency* of *two*.

It will be seen from the foregoing examples that the theory requires that:

1. When an element exhibits multiple valency, the several values of the valency must differ successively by two.

2. When an additional electron in an atom becomes a valence-electron, the valency of the atom must increase by two.

3. A given element must have either even or odd valency consistently in all its compounds

(c) *Valency Relations in the Periodic System*.—On the basis of this theory, it seems reasonable to assign valencies in the periodic system as follows.

Group o	No valency, or even valency
Groups 2, 4, 6, 8	Even valency
Groups 1, 3, 5, 7	Odd valency

Many of the compounds whose molecular formulas are known with certainty, agree with this classification, but there are a number of elements which form compounds of two types, the valency being apparently odd in one and even in the other if we represent these compounds by the simplest possible formulas which will correspond with the percentage composition, but which agree with the theory if the simple formulae of the compounds of one type are doubled As the theory indicates that the valency of a given element should remain consistently odd or even in all its compounds, it becomes necessary in these cases to know the molecular weights of the compounds in question, in order to determine the correct molecular formulas Among these apparent exceptions are the salts of copper and mercury, which will be especially discussed

The helium group includes those elements, the atoms of which are "complete" or perfect" electron systems and which are, therefore, capable of existing in the free or uncombined state, showing no tendency to form doubled systems

If the elements of this group showed any tendency to combine with others, we might expect combination to occur with elements having even valency, most readily perhaps with those which normally occur in the monatomic state such as mercury, zinc and cadmium, and less readily with other elements of even valency It is therefore an interesting fact that Cooke[1] has found some evidences of the combination of argon with zinc, mercury and selenium, and of helium with cadmium, mercury and selenium

In Group 1, in which the theory requires that the valency should always be odd, we have the alkali metals, copper, silver and gold The alkali metals appear to be univalent in all compounds, at least no difficulty arises from this assumption Gold is either monovalent or trivalent [2]

Silver seems to be monovalent in all its well known compounds Silver iodide occurs in two allotropic forms which might correspond to any two of the formulas $Ag\,I$, $Ag \equiv I$, $Ag\,I = I\text{-}Ag$

Copper, however, offers some difficulties Cuprous chloride, in the vapor state, has the formula Cu_2Cl_2, according to Biltz and V Meyer[3] and V Meyer and C Meyer,[4] while Werner[5] found that the formula was CuCl in organic solvents, and the same was found by Rugheimer and Rudolphi[6]

[1] Z physik Chem , 55, 537 (1906)
[2] Pope and Gibson Trans Chem Soc , 91, 2061 (1907)
[3] Biltz and C Meyer Ibid , 22, 725 (1889)
[4] V Meyer and C Meyer, Ibid , 12, 609 1112 1185, 1292 (1879)
[5] Werner, Z anorg Chem , 15, 565 (1897)
[6] Rugheimer and Rudolphi, Ann , 339, 311 (1905)

in solutions of cuprous chloride in fused bismuth chloride and by Beckmann and Gabel,[1] using quinoline as solvent.

The formulas for cuprous chloride in these two forms can be written ·

$$Cu -- Cl \quad or \quad Cu - Cl = Cl - Cu^2$$
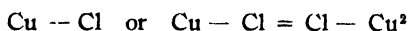
copper being monovalent in both cases.

$$or \quad \begin{matrix} Cl = Cl \\ | \quad | \\ Cu -- Cu \end{matrix} \quad or \quad Cu{\equiv}Cl$$
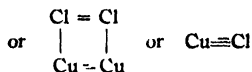
in which copper is trivalent.   (Two of these types may exist as allotropic modifications.)

In cupric chloride, however, the usual formula, $CuCl_2$, would require that the valency of copper should be even, if that of chlorine remains odd, so that to make this compound conform to the new theory, which indicates that copper should have odd valency, the formula must be doubled, which may be done in various ways.
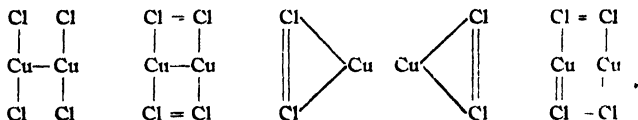
There seems to be no evidence to support any of these formulas, but on the other hand, no definite experimental evidence was found to show that copper is ever bivalent, and we shall have to await the determination of the molecular formula of some cupric compound before we are able to decide the question.

On the basis of this theory, cupric compounds should have the general formula Cu_2X_4 in the undissociated state, if the valency of copper is odd.

In the second group, which should exhibit even valency, no special difficulties are encountered until we come to mercury. In mercuric compounds there seems to be little doubt that the mercury is divalent, the best evidence being the formation of compounds of the type HgX_2 with the organic radicals.   In regard to mercurous compounds, there appears to be some doubt still, although much work has been done on the constitution of mercurous chloride.   It was at one time supposed, on the basis of vapor density measurements, that calomel had the formula HgCl, but it was later shown that on vaporization the salt was decomposed into $HgCl_2$ and Hg, which gave a vapor density corresponding to HgCl.   Baker,[3] however, showed that calomel vapor in the absence of water had the formula Hg_2Cl_2.

[1] Beckmann and Gabel, *Z. anorg. Chem*, **51**, 536 (1906).
[2] J Newton Friend, "Theory of Valency," p 61 (1908)
[3] Baker, *Trans Chem. Soc*, **77**, 646 (1900).

With only these data, mercury in calomel can be represented as either monovalent[1] or divalent

$$Hg — Cl = Cl — Hg \quad or \quad Cl — Hg — Hg — Cl$$
$$(I) \qquad\qquad (II)$$
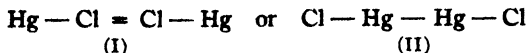
I am of the opinion that mercury in calomel is divalent and that the formula of calomel should be written

$$Hg\!\!\diagup\!\!\diagdown\!\!Hg$$

(III)
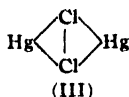
This formula would easily account for the decomposition of Hg_2Cl_2 into $HgCl_2$ and Hg, as an atom of mercury simply splits off, leaving $HgCl_2$, according to the equation
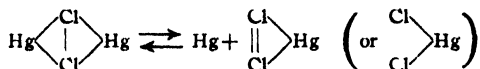
Moreover, a molecule of Hg_2Cl_2 constituted according to Formula III could not readily split into 2 HgCl, which again agrees with experimental results

There is, however, no evidence yet which will decide this question, but it may be said that our apparent inability to prepare mercurous salts or organic derivatives of the type HgX where X is a monovalent element or radical, is presumptive evidence that mercury does not have unit valency, and that we are justified in considering mercury no exception to the theory

The other groups could be discussed in the same way and apparently show no special contradictions to the theory   In cases such as the halogen salts of gallium and indium, in which the evidence showing that the valency of the metal may be both odd and even, rests on vapor-density measurements, I think, in view of the work of Baker on mercurous chloride, that more remains to be done, before we can accept formulas derived in this way as evidence against the theory

Applications of the Theory.

(a) *Mechanism of Reactions* —Let us consider a simple reaction, such as the combination of hydrogen and chlorine   Reaction occurs only during collisions, or when the molecules come within a certain distance of each other, and may be conceived to occur in either of two different ways

(1) The valence-electrons in two adjacent molecules may simultaneously shift their positions to form the new compound   The method by which the shifting could take place is illustrated in Fig 9, a, b, and c

Fig. 9a shows a hydrogen molecule with the valence-electron in the middle of its path of oscillation, and also a chlorine molecule of exactly similar structure   In Fig. 9b the valence-electrons are at opposite ends of

[1] J N Friend, "Theory of Valency, p 67 (1908)

their paths, so that each hydrogen atom is adjacent to an oppositely charged atom. If the valence-electrons are in this relative position at the moment when a collision occurs, conditions are very favorable for combination, and, since hydrogen chloride is a more dynamically stable electron system than either hydrogen or chlorine, the valence-electrons will oscillate in new paths, as in Fig. 9c, thus forming the new compound, HCl.

The position illustrated in Fig. 9a is not the only one favorable for reaction, since any position in which both atoms of a chlorine molecule are in contact with the corresponding atoms of a hydrogen molecule would be favorable. Not every colliding pair of molecules will, at the instant of collision, be in the position most favorable for reaction, hence the number of collisions resulting in chemical combination would be only a certain percentage of the whole number of collisions.

The increase in the rate of reaction caused by raising the temperature would be due to an increase in the number of collisions per second. The increase in the reaction rate caused by light is perhaps due to a sort of polarization of the molecules which arrange themselves in similar positions along the direction of the light rays, or the valence-electrons may be constrained to move in a particular way which favors reaction during collision.

(2) Another explanation of the mode of reaction is the following: a certain number of the collisions between the molecules of a gas may result in dissociation, and in a mixture of hydrogen and chlorine the ions or partial atoms thus produced would recombine to form HCl. On this view, the effects of heat and light are merely to increase dissociation; the former by increasing the velocity, and hence the collision rate; and the latter by influencing the motion of the valence-electrons within the molecules.

A chemical reaction, then, is nothing more than the readjustment of the paths of oscillation of valence-electrons between the atoms of contiguous molecules.

(b) *Tautomerism.*—On this theory the "wandering" of hydrogen in an organic compound, and the equilibrium between tautomeric substances can be explained as a special kind of chemical reaction. As an example take the case of acetoacetic ester. This substance exists in two forms—the enol form:

$$CH_3 — C(OH) = CH — COOC_2H_5$$

and the keto form:

$$CH_3CO — CH_2 — COOC_2H_5$$
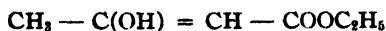
Writing these formulas with the valence-electrons indicated we have for the enol form, Fig. 10, and for the keto form Fig. 11. In the enol form the hydrogen of the hydroxyl group, and perhaps the hydroxyl group itself, has a certain freedom of motion, and at some particular instant the molecule will have the configuration shown in Fig. 10, in which the hydrogen is

nearly in contact with the α-carbon atom. If now a readjustment of the motions of the valence-electrons should occur as indicated by the small arrows, so that the hydrogen becomes attached to the α-carbon atom, and the oxygen attached to the β-carbon becomes double-bonded, we should have the keto form, Fig. 11.

The reverse transformation could be explained in a similar way. According to this view, the wandering of hydrogen is simply a change of path of certain valence-electrons in the molecule. Other types of tautomerism could be explained similarly.

(c) *Conduction in Metals.*—Consider a solid mass of silver, and assume that its molecules are diatomic, two atoms of silver being connected by a single oscillating valence-electron.

If two molecules are close together we may conceive that a species of chemical reaction may occur, involving a shifting of valence-electrons, and forming new molecules as in Fig. 12.

If we consider a constant shifting and oscillation of valence-electrons to be taking place in this way in a mass of metal, we have an explanation of the freedom of electrons, upon which the conductivity of a metal is supposed to depend. According to this view, the number of "free" electrons will be of the same order as the number of molecules in unit volume, but the *time* that the electrons are actually free may be very small or zero. When a potential difference is applied to a piece of metal, the electrons are constrained to drift in one direction, and we have an electric current.

The way in which the electrons may drift in one direction in an electric field, while still functioning as valence-electrons is illustrated in Fig. 13, in which a chain of molecules is shown in five successive conditions.

In position A each of the molecules 1-2, 3 4, 5-6 and 7-8, has its valence-electron at the point of contact between the atoms as shown. In position B, the valence-electrons have moved toward the positive pole, and the atoms have become ions of opposite signs. The ions 1, 3, 5, and 7 are positive and drift toward the negative pole, or to the left in the diagram, while the ions 2, 4, 6 and 8 are negative and move to the right. The mean free paths of these ions are very short, and the ions 2 and 3 very soon come together as in C; and the valence-electron of 2, which continues to drift to the right, becomes the bond of the molecule 2–3. The other pairs of ions in the same way form the new molecules 4–5, 6–7, etc.

The motion of the valence-electrons toward the positive pole continues and we soon have the condition shown in D, in which the atoms 1, 3, 5 and 7 have now become negative ions, and started to move toward the positive pole. Finally, we have the condition shown in E, which is the same as in A except that the valence-electrons have each advanced a certain distance.

We see, therefore, that the electrons do not really have to be "free,"

in the sense of being outside of the molecules, in order that a substance should conduct. It is only necessary that their direction of movement be brought under control.

We have now gone through a complete cycle of changes in which each electron has moved toward the positive pole a distance equal to twice the diameter of an atom plus the mean distance between two molecules, and at the same time each atom has moved half the distance separating two molecules and back again.

Thus, a directional *drift* of the valence electrons is accompanied by an oscillation of the atoms, and we can construct on this basis a more or less clear mental picture of the thermal phenomena accompanying the flow of electric currents in metals.

An electron ᵣ ably encounters little or no resistance to its motion while inside of, forming part of an atom, so that electrical resistance is due mainly tᵣ ᵣ molecules not being in contact, and thus being obliged to oscillate in oᵣ to allow a drift of the electrons in the manner illustrated. Cooling a metᵣ wers its resistance by bringing the molecules closer together and reduᵣᵣng the amplitude of oscillation of the atoms. At absolute zero, when there is no motion of the atoms, and they are very close together, the electrons can move in approximately straight lineˢ without hindrance and the conductivity is very high.

Alloys present some interesting phenomena. If compounds are formed, the molecules are unsymmetrical and are consequently less often in positions favorable to an interchange of electrons, which presumably will seldom occur, except when the new molecules formed by the reaction are like the original ones. The small percentage of opportunities for the transfer of electrons, causes such an alloy to have a high resistance. The more complicated the molecule is, the higher the resistance should be. If the constituent metals form no compound, the conductivity of the alloy should be quite high, and should correspond approximately to that calculated from its composition.

The small temperature coefficient of resistance of alloys may be explained as follows:

The metallic compound dissociates with rise of temperature so that the alloy is a mixture of pure metals and a compound of them. As the temperature rises, the composition approaches that of a mixture of the two pure metals, which has a lower resistance than that of the compound. At the same time the resistances of the pure metals themselves are increasing, and this opposes the diminution of resistance due to dissociation, so that the net rate of change may be very small.

(*d*) *Association.*—Association may be defined broadly as a combination of two or more molecules to form a single complex molecule. In a general way, it includes not only the formation of complex molecules from organic

hydroxyl compounds, the addition of water to salts as water of crystallization, the addition of halogen hydrides to ethers to form oxonium salts, all of which probably involve an increase in the valency of oxygen from two to four, but also the formation of double salts by the union of two or more single salts. The increase of valency can take place as illustrated in the case of formation of $ZnCl_2$ from Zn and Cl_2, or of $AuCl_3$ from AuCl and Cl_2.

The formation of "intermediate compounds" or addition products during a chemical reaction can be readily explained by assuming that extra valencies are momentarily brought into action to form unstable associated molecules.

(e) *Dissociation and Conduction in Electrolytes.*—Consider a solution of a simple binary compound; for example, hydrochloric acid. In aqueous solution the molecules are, according to the electrolytic dissociation theory of Arrhenius, largely dissociated into positive hydrogen ions and negative chlorine ions. These are considered to differ from the ordinary atoms only by being charged. When the charges are given up at the electrodes during electrolysis, the ions become converted to *uncharged atoms*. The electrolytic dissociation theory is somewhat vague as to the origin of the charges on the ions, as well as to the mode by which *molecules* are formed from uncharged atoms at the electrodes.

According to the new theory, the dissociation of the molecule is a division in such a way that the valence-electron forms part of the negative ion, while the positive ion consists of a partial or incomplete atom, as shown diagrammatically in Fig. 14.

The charge of a monovalent ion would therefore be $\epsilon/2$, or half the charge of a single free electron, while the charge of a divalent ion would be ϵ, etc.

Omitting, for the present, any speculation as to the primary cause of dissociation, the explanation of the phenomena at the electrodes is as follows:

The current in the hydrogen chloride solution consists of a stream of chlorine ions moving to the anode, and of hydrogen ions moving to the cathode. In order that molecular hydrogen may be formed and set free at the cathode, one electron must be supplied to every pair of hydrogen ions arriving at the cathode, and this is supplied from the stream of electrons which constitute the current in the wire leading to the cathode, thus liberating molecular hydrogen. At the anode, very similar phenomena occur; every pair of chlorine ions reaching the anode must lose one electron in the process of forming molecular chlorine, this electron passing into the conducting wire.[1]

The process of discharging ions at the electrodes and forming neutral

[1] Compare P. Achalme, *Compt. rend.*, 154, 647–99 (1912).

molecules should be capable of explanation in such a way as to make clear the nature of polarization and of decomposition voltage, neither of which have yet had a wholly satisfactory explanation.

The following is an explanation of these phenomena by the new theory: In a hydrochloric acid solution the negative chlorine ions move toward the anode and, if the voltage is not too high and the material of the anode does not combine readily with chlorine, the surface of the anode soon becomes covered with a molecular layer of these ions, and is said to be polarized. To discharge these ions, the potential difference at the electrode must be great enough to pull the valence-electrons away from the atoms.

If a potential greater than this value (commonly called the "electrode single potential") be applied, the negative chlorine ions give up their valence-electrons, which then pass off into the wire leading from the anode, and the negative chlorine ions, upon losing valence-electrons, according to the theory become *positive* ions. The positive chlorine ions thus produced would immediately begin to move away from the anode, and would soon combine with approaching negative chlorine ions to form neutral molecules of chlorine gas.

At the surface of the anode during electrolysis, there would be a layer of ions undergoing a change of sign from negative to positive, while, at a short distance away from the surface of the anode, there would be an advancing layer of negative ions, and between them a reaction zone where neutral molecules are formed.

The phenomena at the cathode would be quite similar to those at the anode.

Fig. 15 shows a polarized anode covered with a molecular layer of negative chlorine ions.

Fig. 16 shows an anode at which the potential is high enough to remove electrons from the negative ions, and shows positive ions moving away from the electrode just after losing electrons, also a molecule of Cl_2 escaping.

The electrode single potential depends on the nature of the electrode material, and will be the algebraic sum of the potential representing the attraction of the electrode material for electrons, and of the force necessary to remove an electron from a negative ion at the anode, or to add an electron to a positive ion at the cathode.

Just as many electrons are passing into the solution at the cathode as there are leaving at the anode. Thus, the theory of the mechanism of conduction in electrolytes is in complete harmony with the theory of a current in a metallic conductor as a stream of electrons.

Let us now consider the special case in which the "positive" element of the compound forms monatomic molecules. If we take zinc chloride for an example; the salt, in solution dissociates as follows: $ZnCl_2 = Zn + 2Cl$

so that we have a divalent positive zinc ion and two negative chlorine ions, the valence-electrons remaining with the chlorine ions. At the anode, the chlorine ions combine in pairs to form chlorine molecules, and, for each molecule which is formed, one valence-electron is set free and passes into the metallic circuit. At the cathode the conditions are somewhat different. Each zinc ion has a double charge $(2 \times \epsilon/2 = \epsilon)$ and hence requires one electron to convert it into a neutral atom. Each zinc ion, therefore, receives one electron at the surface of the cathode and becomes free metallic zinc in the monatomic state. If zinc in the free state were diatomic, then two zinc ions would unite with two electrons and form a binary molecule.

(f) *Dissociation and Conduction in Gases.*—In an undissociated gas, a free and continuous interchange of electrons between molecules, as in a metal, is impossible, because the molecules are too far apart, so that a gas or vapor is ordinarily non-conducting unless free ions are produced in it by Röntgen rays, ultraviolet light radiation from radioactive substances, or an electrostatic field.

Consider the ionization of a simple binary gas molecule, such as that of hydrogen. According to the new theory, two kinds of dissociation are possible, which I shall call partial and complete dissociation.

(a) Partial dissociation. The molecule can split into two "atomic ions," the positive ion being a "partial atom" *without* the valence-electron, and the negative ion being a partial atom *with* the valence electron. A hydrogen molecule which has undergone partial dissociation in this manner may be represented as in Fig. 18.

The charges on these atomic ions will be $+ \epsilon/2$ and $- \epsilon/2$, respectively, if ϵ is taken as the charge of a single free electron.

(b) Complete dissociation. The molecule can split into three ions, the two "partial atoms" of hydrogen becoming positive atomic ions, each having a charge of $+ \epsilon/2$, while the valence-electron becomes a negative ion with the charge $- \epsilon$. A molecule dissociated in this way can be represented as in Fig. 19.

What determines the type of dissociation which takes place when a gas is ionized? A somewhat analogous case is that of the dissociation of a dibasic acid in aqueous solution which forms first a single hydrogen ion, and a complex negative ion, which is itself further dissociated in more dilute solutions, both types obeying the law of mass action.

If we assume that a gas under the influence of an ionizing agent is subject to laws of equilibrium similar to those that apply to an electrolyte which is being ionized by the dissociating agent, water, the line of reasoning is as follows:

The two types of dissociation may be represented as reversible reactions, thus

$$HeH \rightleftharpoons H^{\cdot} + He'$$
$$HeH \rightleftharpoons H^{\cdot} + H' + \epsilon''$$
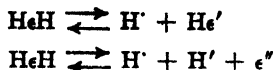
The nature and extent of the ionization produced in a gas when it is in a steady state, under the influence of an ionizing agent, will depend upon the frequency with which collisions causing recombination occur, that is, upon the pressure of the gas. At extremely low pressures, dissociation should be complete and the negative ions should consist of electrons only, while at higher pressures partial dissociation will predominate, and the ions will be mostly "atomic ions"[1] of both signs.

Experimental evidence shows that positive and negative ions in a gas differ in size and that this difference becomes much greater for low pressures of the gas, and that at low pressures the negative ion is identical with the electron. The change in size of the negative ion is quite marked at 10 mm. pressure. The positive ion is always atomic in size, even at a low pressure of the gas.

The commonly accepted theory seems to be that at high pressures the negative ion is an electron to which a cluster of molecules has become attached, and that at low pressures the electron sheds the clusters, and the difference in size and velocity is supposed to be explained in this way, but I believe that the above explanation agrees with the facts just as well.

At moderate pressures, therefore, according to our theory, there should be, in an ionized gas, two kinds of negative ions, viz., "atomic ions" and electrons, and consequently the experimentally determined values of e/m for the negative ion, being average values for all the ions present, should vary with the pressure of the gas between certain limits, which for hydrogen would be 1.7×10^7 and 10^4 (electromagnetic units). The charge on a gaseous ion should also appear to be a variable depending on the pressure, if determined from measurements on a large number of ions at once, as is done by the "cloud method."

At moderate pressures the velocities of positive and negative ions are found experimentally to be *nearly* equal. This agrees with the theory, since the two kinds of "atomic ions" should have the same mass. Since, however, a certain proportion of the negative ions will be electrons, with much higher velocity than the atomic ions, the *average* velocity of the negative ions should be somewhat greater than for the positive ions. Here again, experimental results agree with the theory.

Any element having odd valency should, in the gaseous state, show a perceptible increase in electrical conductivity when dissociated by heat, because the free atoms must necessarily be charged.

The elements of the helium group, which occur in the free state in the

[1] For the sake of clearness, the term "atomic ion" is proposed, to distinguish such ions as $H^{\cdot}$ and He' from electrons.

uncharged monatomic condition, would be expected to become divalent if ionized. Rutherford and Geiger's value of 9.3×10^{-10} E. S. U. for the charge on an α-particle is approximately twice Millikan's value for the unit ionic charge, and agrees with the theory. A neutral helium atom by losing a single electron would become a positive ion with a double charge (See Fig. 20), and *vice versa*, when an α-particle gains an electron it becomes an uncharged helium atom. This probably occurs during many radio-active changes.

(*g*) *The Charge and the Apparent Mass of an Electron.*—The charge on a negative ion in a gas at moderate pressures has been determined many times and in many different ways, but the charge on an *electron* has not yet been measured. It is commonly, but without warrant, assumed that the two are equal, and many workers who have determined simply the charge on a gaseous ion use the term *ionic charge, unit charge,* and *electron charge* as though they were synonymous. Some confusion exists because the same symbol is used both for the ionic charge and the electron charge, but, since these quantities are not known to be equal, I would urge that the symbol ϵ be used only for the charge of a single free electron.

My theory seems to require that the charge of an electron should be twice as great as that of an univalent ion, or if the electron charge be taken as a unit and represented by the symbol ϵ, the charge of a univalent ion will be $\epsilon/2$, or *half the unit charge.* Taking Millikan's value[1] for the *ionic charge, e,* we should have for the electron charge, $2 \times 4.774 \times 10^{-10}$ $= 9.548 \times 10^{-10}$ E. S. U.

This point has an important bearing on the value of the apparent mass of an electron, which is usually calculated from the following considerations:

ϵ/m for cathode rays (free electrons) $= 1.7 \times 10^7$

E/M for hydrogen ions in electrolysis $= 10^4$

Now the relation of m to M depends on the relation of ϵ to E. The minimum charge on a negative ion in a gas at ordinary pressure seems, beyond doubt, to be equal to the charge on a hydrogen ion in electrolysis, but J. J. Thomson,[2] assumes that the charge on a cathode-ray particle (corpuscle) is equal to the charge on a negative gaseous ion, and that, therefore, $\epsilon = E$ which leads to the result that $m = 1/1700 \ M$. According to my theory $E = \epsilon/2$, hence $2E/M \cdot m/\epsilon = 1/850$, or $m = 1/850M$.

We have the following values:

ϵ, the electron charge $= 9.548 \times 10^{-10}$ E. S. U.

e, or E, the univalent ionic charge $= 4.774 \times 10^{-10}$ E. S. U.

m, the apparent mass of an electron in cathode rays $= 1 \ 65 \times 10^{-24}/850$ $= 1.94 \times 10^{-27}$ gram.

[1] *Phys. Rev.*, [2] 2, 109–43 (1913).
[2] "Conduction of Electricity through Gases," 2nd Ed., p. 160.

Summary.

The theory assigns to the "bond" a physical meaning, the oscillating valence-electron; and this idea is shown to be in harmony with recent theories of the structure of matter.   It explains a number of phenomena in a fairly satisfactory way.

Valency is the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a relatively stable, electrically neutral system.

The valence-electrons oscillate periodically between the atoms which they unite.

Valency is, therefore, a purely mechanical result of the dynamic relations between molecules and the atoms of which they are composed.

The valency of an atom in a state of combination with other atoms is simply a numerical quantity, neither positive nor negative, but the valency of a radical or an ion may be positive or negative.

Explanations are given of the mechanism of chemical reactions, tautomerism; conduction in metals; association; dissociation and conduction in electrolytes and gases.   The following deductions from the theory are made:

Uncharged free atoms can exist only when the element belongs in an even group of the periodic system.   Free atoms of elements of odd valency can exist only as ions having charges which are odd multiples of the unit ionic charge.

Elements belonging to odd groups of the periodic system will have odd valency, while elements of even groups will have even valency.

Valency varies in steps of two, being always even or always odd for the same element.

The unit electric charge or the charge of an electron is twice the ionic charge or 9.548×10^{-10} E. S. U.

The apparent mass of the electron in cathode rays is $1/850$ of the mass of a hydrogen atom.

RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO,
SCHENECTADY, N Y

THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.

BY WILLIAM BARLOW AND WILLIAM JACKSON POPE
Received January 5, 1914.

In a recent paper,[1] Professor Theodore W. Richards criticizes adversely the work which we have done on the relationships existing between crystal structure and chemical constitution and arrives at the conclusion that many of our arguments are fallacious and that our theoretical deductions must be rejected.   We welcome this criticism, not only because of its

[1] THIS JOURNAL, **35**, 381 (1913).

studied impartiality and its appreciation of the questions at issue, but also because it furnishes us with an insight into the sort of difficulties which the chemical reader is likely to encounter in studying the somewhat complex geometrical and crystallographic problems involved. As we are not in agreement with Richards' presentation of our position (p.383) we may be permitted to state our own case.

We make the following brief statement of the position attained by the study of crystal structure before either party commenced work upon it, previous to discussion whether Professor Richards' criticisms of our mode of treating the subject are legitimate and comparing the fecundity of our mode of treatment with that of his method.

All the properties of crystalline solids harmonize with one simple assumption as to the manner in which the parts of the structure are arranged; this assumption is that the structure is a geometrically "homogeneous" one, namely, a structure the parts of which are uniformly repeated, corresponding points having a similar environment throughout the assemblage.[1] The determination of the number of types of homogeneous structure, including all possible arrangements of points in space, was definitely completed before the publication of the first paper above mentioned. The 230 types recognized, distinguished from one another by the different modes of repetition of their parts, are found on examination to fall under 32 classes of crystal symmetry discriminated by the crystallographer. The limitation of the possibilities of solid crystalline arrangement to 230 types obviously marks but one stage in the determination of crystal structure and throws no direct light on the relationship which exists between crystal structure and chemical constitution; the conception of the closest-packing of the atoms, introduced at a later date, is not a factor in the purely geometrical problem of determining the variety of types of arrangement described.

Regarding the geometrically homogeneous character of crystalline solids as proved, it follows that the units of any particular solid crystalline substance must be regarded as centered at the points of a homogeneous point-system of one of the 230 types. We conclude, further, that all identically similar atoms present in a crystalline assemblage of molecules must be conceived as centered at the points of some such homogeneous point-system, or systems. The structure of a crystalline compound is thus to be regarded as built up of a number of interlaced, congruent point-systems, the points of each component system being the centers of one particular set of the component atoms. The number of component point-systems is thus the same as the number of kinds of atoms, distinguishable materially or by position, contained in the chemical molecules of which the substance is composed.

[1] Compare Barlow and Pope, *J. Chem. Soc.*, **89**, 1676 (1906).

So far we have dealt with conclusions which have been long accepted or with such simple deductions from those conclusions as will hardly provoke dissent; proceeding from these conclusions as a basis, we now describe our method of attacking the problem involved in the relation between crystal structure and chemical constitution.

We make the fundamental assumption that the crystal structure affected by a substance is an equilibrium arrangement of the atoms composing the material, each atom being regarded as a center of opposing and attractive forces of the nature of kinetic repulsion and gravity attraction; the particular set of intercalated point-systems representing a specific crystalline solid is thus an equilibrium arrangement of the forces resident in the component atoms, one atom being centered at each knot of the set in point-systems. The condition thus conceived may be easily visualized in connection with the crystalline form of a monoatomic element, in which, presumably, all the component atoms are identically similar and are similarly placed with respect to the crystal structure. The crystalline condition of such an element is to be regarded as one of equilibrium between forces of attraction and repulsion emanating from, or referable to, a single flock of points homogeneously arranged in space, namely, of points of a single homogeneous point-system; the consideration of this simple case reveals the need of a method for determining what is the equilibrium arrangement of the flock of Boscovichian points exercising identical mutual influence. Our method of solving the problem thus presented introduces the conception of closely packed spheres of influence above referred to; it assumes that the forces present obey some inverse distance law operating similarly and uniformly in every direction from each similar center and treats the influence exerted by other centers immediately surrounding any selected center as so much greater than the influence exerted by centers further removed that their influence may be regarded as negligible.

The equilibrium arrangement of the set of points thus similarly endowed with kinetic energy and attracting each other with a force of the gravity kind, will, according to the conception referred to, be that homogeneous arrangement which, with a given density of distribution of the points, gives a maximum distance between nearest points.

Since the points are equidistant, equal spheres can be described with centers at these points of such a magnitude as to be in contact; it can be shown that, with a given density of distribution of the points, a maximum distance between nearest points and consequently a maximum volume for the spheres, or, in other words, closest-packing of the spheres, will be presented when each sphere of the assemblage, regarded as indefinitely extended, is in contact with twelve others. Two different kinds of arrangement of twelve spheres about a single sphere are, however, equally

available for this; the prescribed homogeneity of arrangement can be
achieved with either of these kinds present alone or with a symmetrical
intermixture of them.

Of the two closest-packed homogeneous assemblages in which one or
other of these two kinds of arrangement is alone present, one has cubic
symmetry, and is represented in (Fig. 1) while the other (Fig. 2) possesses
hexagonal symmetry.
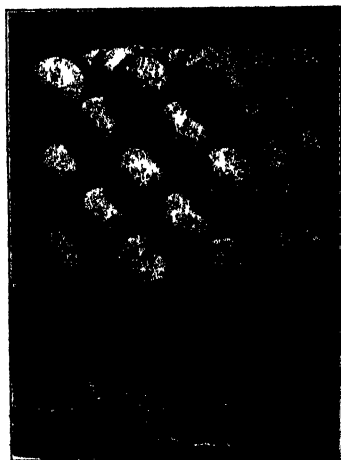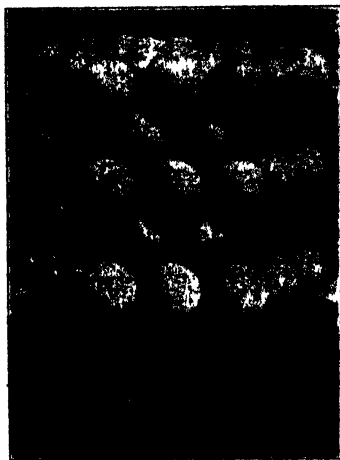
Fig. 1.   Fig 2.

If, in each of these two assemblages, tangent planes are drawn at all
the points of contact of the spheres, each sphere becomes enclosed in a
circumscribing 12-faced polyhedron.   As a result of the operation of the
inverse distance law the surfaces of the polyhedra thus derived mark the
boundaries of the domains of predominant influence of the individual
atoms, each point in space experiencing under this law predominant influ-
ence from the atomic center nearest to it.   Points on the boundary planes
of the polyhedral cells are equidistant from two or more centers.

Of the elements which have been crystallographically examined,
50% are cubic and 35% are hexagonal; we have suggested that the crystal
structures of these 85% of the elements are represented by the two closest-
packed assemblages just described, or by some very simple combination
of them.   We have also shown that the remaining elements, which crys-
tallize in systems of lower symmetry, present crystallographic peculiarities
which lead to the conclusion that their crystal structures are represented
by slight distortions either from cubic or from hexagonal symmetry;
we have also indicated that this distortion may be the geometrical conse-

quence of the aggregation of atoms to form polyatomic molecules and, in the case of carbon, have shown that a slight distortion of the hexagonal assemblage, which might be caused by atomic aggregation, would account for the crystalline form of graphite and for the oxidation of this allotrope of carbon to mellitic acid. We have also pointed out that the crystalline form of an element which departs from the simple cubic or hexagonal type of symmetry is always colored while those modifications which conform to the two simpler types of symmetry are in general colorless; thus, the colorless diamond and ordinary phosphorus are cubic, while the black graphite and red phosphorus are respectively monosymmetric and ortho-rhombic.[1]

A perusal of our published papers will show that the correspondence between the assemblages which have been constructed and the crystalline forms of the elements is of a highly quantitative character. But probably Richards will agree with us in this part of our work, since he, like ourselves, is prepared to refer the departure from the symmetry of the two simple forms of assemblage above described, which are presented by about 15% of the elements, to a modifying effect traceable to the formation of groups or atomic aggregates; in view, however, of the detail in which we have discussed the subject, his suggestion that we "do not seem to have attached quite enough weight to the fact that elements are not always necessarily composed of monatomic molecules" (p. 387), appears of obscure applicability. In any case the validity of our valency volume law does not come into question with a crystalline element and when Richards says "it appears that the theory of compressible atoms explains the crystalline form of the cubic and hexagonal elements as well as Barlow's and Pope's theory" (p. 388) we do not know what theory, as distinct from our own, he can have in mind.

It will have been seen that we allot to each atom present in crystalline structure, a point, which may be taken as representing the center of gravity of the atom, and a plane-faced polyhedral domain, termed the sphere of atomic influence, which on our conception of equilibrium represents the region over which its centered atom exerts predominant influence by reason of its attractive and repulsive forces. Prof. Richards has well indicated our relative positions by the following statement:[2] "the so-called 'sphere of influence' of the atom is the actual boundary by which we know the atom and measure its behavior. Why not call this the actual bulk of the atom?" In accordance with this idea, Prof. Richards translates our term "sphere of atomic influence" by "volume of the atom" or by "compressible atom." These several terms are, for his and our purposes,

[1] *Proc. Roy. Soc. (Dublin)*, **8**, 535 (1897); *J. Chem. Soc.*, **91**, 1159 (1907); *Ibid.*, **89**, 1741 (1906); *Reports Chem. Soc.*, **5**, 270 (1908).

[2] Richards, "The Faraday Lecture of 1911;" *J. Chem Soc.*, **99**, 1206 (1911).

quite freely interchangeable. Richards suggests, however, because his atomic domains are compressible while the spheres representing atoms which we have used are said by us to be incompressible, that the respective views as to the nature of matter are antagonistic.

We must point out that this suggestion is based upon an entirely false conception of the views of the two parties. Richards, in common with us, adopts the hypothesis that in a crystalline solid the spheres of atomic influence fill the available space without gaps or interstices; each atomic domain, polyhedral in shape, represents to him an atom and since a substance changes its value on subjection to pressure he necessarily regards the atoms as compressible. We, dealing with a different branch of the subject and using a different terminology, find it convenient to construct models representing the comparatively static conditions prevailing in a crystalline solid under a given fixed set of external conditions; to indicate the mode of constructing the model we have suggested the use of "deformable, incompressible" spheres because, on application of adequate pressure, a mass of such spheres would undergo deformation, without changing in actual volume, and would become converted into polyhedra filling the available space without appreciable interstices. Under the conditions which prevail in our static systems the atoms or atomic domains are incompressible because, by definition, no force is operative to compress them, namely, to diminish their volume. With a change in the conditions external to the atom—change in temperature, passage of the atom from one compound to another, or by the application of external pressure—a dynamic condition is established under which the polyhedral atomic domains will necessarily alter in volume; we have considered at some length, exactly on the lines which Richards appears to approve, the change in volume of the spheres of atomic influence with change of temperature and during passage from one compound to another.[1]

Turning next to what we have called the "valency volume law," it should be remarked that we have not, as Richards suggests, made as our "guiding principle the assumption that each valency in a given compound has essentially the same volume and, hence, that the atomic volumes of combined elements are directly proportional to their valencies" (p. 384); our guiding principle is that in every crystalline solid the system of arrangement of parts is an equilibrium one reached by the operation of centered forces. We do not put the law of valency volumes forward as a mere plausible working hypothesis but have deduced it as an argued conclusion based on the interpretation of the facts. Having deduced the law, we have in our various papers subjected its validity to a series of simple quantitative tests and have thereby obtained abundant confirmatory evidence indicating that the law is quite generally obeyed among crystalline

[1] *J. Chem. Soc.*, **89**, 1679 (1906).

solids. Further, LeBas showed that the molecular volumes of a series of paraffins, determined in the liquid state at the melting points, indicate that the atomic volume of carbon in these substances is four times that of hydrogen, and hence suggested that the valency volume law applies even in liquids.[1] To this Richards retorts (p. 385) that "values calculated on almost any assumption within reason" would also do so. But is this correct? Richards quotes the values for four hydrocarbons stated in LeBas' table, and calculates the molecular volumes on our view (C = 4 times H) and on the one he selects to illustrate his point (C = 2H).

	Observed mol Volume	Barlow & Pope C = 4H	New assumption C = 2H
$C_{11}H_{24}$ .. .	201 4	202 0	203 3
$C_{26}H_{42}$	362 5	363 3	362 3
$C_{27}H_{66}$.	487 4	487 1	486 2
$C_{34}H_{72}$	629 5	629 6	627 6

A short calculation will show that the mean differences between corresponding figures in Columns 2 and 3 is 0.3, while that between Columns 2 and 4 is 1.3; the calculations made according to the results of our conclusions concerning valency volume thus agree four times better with the observed values than do those made on the arbitrary assumption that the atomic volume of carbon is twice that of hydrogen. This result, which becomes far more striking when the values for the whole set of hydrocarbons discussed by LeBas are considered, hardly leads logically to the conclusion that "as an argument in support of the constancy of the valency-volume in any one instance, the table of molecular volumes of hydrocarbons has no significance" (p. 385). The testimony in confirmation of the conclusion that the atomic volume of carbon is about four times that of hydrogen in any given compound becomes overwhelming when the further work of LeBas is considered, namely, that in which he deals with the mass of data collected by Young on the relation between the density of substances at corresponding temperatures.

Large numbers of cases are known in which an obvious relationship exists between the crystalline form of two or more substances, which are chemically related. When the chemical relationship is very intimate, as, say between K_2SO_4 and Rb_2SO_4, close crystallographic similarity in general also exists; the two substances are said to be isomorphous and the axial ratios, representing the comparative dimensions of the crystal structure along three-dimensional coördinates, are nearly the same for the two substances. But in addition to cases of isomorphism, numerous instances are known in which both the chemical and crystallographic similarity are less marked, although still perfectly distinct; substances of this kind are described as morphotropically related and; previous to our work, no clue was available by means of which the morphotropy could be eluci-

[1] *J. Chem. Soc.*, **91**, 112 (1907); *Phil. Mag.*, **14**, 324 (1907); **16**, 60 (1908).

dated. Thus, *d*-camphoric anhydride, $C_{10}H_{14}O_3$, is morphotropically related to the compound which *d*-camphoric acid forms with acetone, $C_{10}H_{16}O_4.^1/_2(CH_3)_2CO$; both substances are orthorhombic and the axial ratio, c/b, is nearly the same in both. If the valency volume law is valid it might be expected to furnish a clue to this mysterious morphotropic relationship in the following manner.

The law indicates that in each of these substances the atomic volumes of carbon, oxygen and hydrogen are in the ratios of 4 : 2 : 1; we, therefore, represent the unit of each compound by a rectangular block of volume equal to the sums of the respective component valencies (the so-called valency volume = W) and calculate the rectangular dimensions of these blocks, taking them as in the ratio expressed by the axial ratios. The three rectangular dimensions, x, y, and z, we term the "equivalence parameters," and they, with the axial ratios, $a : b : c$, are stated in the following table:

	W.	a : b : c	x : y : z
d-$C_{10}H_{14}O_3$	60	1.0011 : 1 : 1.7270	3.2654 : 3.2618 : 5.6331
d-$C_{10}H_{16}O_4.^1/_2(CH_3)_2CO$..	74	1.2386 : 1 : 1.7172	4.0435 . 3.2646 : 5.6060

It will be seen at once that the approximation between the axial ratios c/b is translated in the equivalence parameters by an approximation between the respective values for y and z; a little consideration will show that if the units of volume selected in the two cases differed markedly from the relative proportion of the values for W, the valency volume, this correspondence could not occur. We conclude that, unless the morphotropic relationship is wholly fortuitous, it is the result of the operation of the valency volume law.

A remarkable morphotropic relationship has long been recognized between the minerals of the so-called humite group.[1] The monosymmetric mineral chondrodite, $Mg_3(SiO_4)_2.2Mg(F,OH)$, the orthorhombic humite, $Mg_5(SiO_4)_3.2Mg(F,OH)$, and the monosymmetric clinohumite, $Mg_7(SiO_4)_4.-2Mg(F,OH)$, in each of which the interaxial angle $\beta = 90°$, are related in such a way that, while the axial ratio, a/b, is practically the same in all, the ratio, c/b is approximately in the proportion of 5 : 7 : 9 for the three substances respectively. Assigning to Mg, Si and O, valency volumes of 2, and to F and H, volumes equal to unity, and assuming for the sake of simplicity, that the isomorphously replaceable fluorine and hydroxyl are present in equivalent quantities, the valency volumes corresponding to the above compositions become 34, 48 and 62, respectively; these values are roughly in the proportion 5 : 7 : 9 shown by the axial ratios, c/b.

The nature of the morphotropic relationship is exhibited more accurately in the equivalence parameters stated at the beginning of the accompanying table; while the values for x and y are practically constant for the three

[1] Penfield and Howe, *Z. Kryst. Min.*, **23**, 78 (1894).

minerals, the whole effect of the change in valency volume falls on the axis c. This is also shown by the constancy of the values z/W, which indicates that the length of the axis c is very closely proportional to the valency volume.

Mineral	W	a		b	.	c		x		y		z		z/W
Chondrodite	34	1	08630	1		3	14472	2	3367	2	1510	6	7644	0 19895
Humite	48	1	08021	1		4	40334	2	3343	2	1610	9	5155	0 19824
Clinohumite .	62	1	08028	1		5	65883	2	3384	2	1646	12	2491	0 19756
Prolectite	20													
Observed		1	0803	1		1	8862	2	3130	2	1411	4	0385	0 19977
Calculated		1	0818	1		1	8618	2	3365	2	1589	4	0211	0 19968
Forsterite:	14													
Observed		0	9296	1		1	1714	2	3426	2	1778	2	7442	0 19601
Calculated		0	9240	1		1	1741	2	3365	2	1589	2	7433	0 19595

The minerals chondrodite, humite and clinohumite have been very accurately determined and, as will be seen, form a kind of homologous series in which the homologous increment has the composition Mg_2SiO_4; subtracting this increment from the composition of chondrodite, the residue $MgSiO_4 \cdot 2Mg(F,OH)$ is left. This is the composition attributed to prolectite[1] which may thus be regarded as the first member of the humite series. Further, the mineral forsterite, Mg_2SiO_4, has the composition of the homologous increment of the series.

Prolectite and forsterite have been less well determined than the preceding three minerals but, on the basis of the valency volume law, we can calculate the axial ratios and equivalence parameters of the two substances in question from the more accurate data available for the first three. The table gives this calculated data together with the observed axial ratios and the equivalence parameters calculated therefrom. The correspondence between the observed and calculated values is very close; it is seen that the directions a and b in forsterite correspond to the equivalence parameters y and x, respectively. For the purpose of these calculations the only modifications which have been made in the published axial ratios of the five minerals is that, in the case of forsterite, unit length along the axis b has been divided by two.

We have given, above, two out of a great number of available instances of the service rendered by the equivalence parameters in illustrating the valency volume law and in giving a quantitative significance to morphotropy. In addition to the cases which we have ourselves exposed, Armstrong and Rodd[2] and Jerusalem[3], Colgate and Rodd,[4] and Armstrong,[5]

[1] Sjogren, Z Kryst Min , 26, 103 (1896)

[2] Proc Roy Soc , 87A, 204 (1912); 90A, 111 (1914)

[3] J. Chem Soc , 95, 1275 (1909); 97, 2190 (1910); 101, 1268 (1912)

[4] Ibid., 97, 1585 (1910).

[5] Ibid., 97, 1578 (1910)

Glover and Lowry[1] have, with the aid of the equivalence parameters greatly increased our knowledge of the chemical significance of morphotropic relationships.

Professor Richards rejects the equivalence parameters as being a "mathematical device" and because "the facts all seem to be so reasonable and need no preliminary mathematical treatment" (p. 391), but crystallography is an exact science which can only be correlated with chemistry by quantitative methods. His attack on the calculation of equivalence parameters from axial ratios which have been subjected to division of multiplication consists mainly in a restatement of our own preliminary warning concerning their legitimate and illegitimate use and the extent to which importance could be attached to them;[2] although from the nature of axial ratios, their fractionation is often necessary and legitimate operation, we have, in no crucial instance from which we draw a conclusion of importance, made use of axial ratios which have been subjected to modification.

We submit that the method of quantitative treatment which we have devised for the elucidation of the relationship between crystalline form and chemical constitution, the first comprehensive method introduced, has proved so fertile in coördinating the two subjects of chemistry and crystallography that it cannot be affected by adverse criticism of the kind employed by Professor Richards. The subject has been carried too far on a highly quantitative basis to be touched by vague qualitative criticism involving suggestions as to what is "reasonable" or as to what "we should expect." To be successful, the critic must put forward a comprehensive quantitative scheme obviously superior to the one which we have applied to the camphoric acid derivatives and the humite minerals dealt with in the above table, as well as to numbers of other problems involved in our detailed papers.

Several more points still merit mention. The arrangement suggested by Richards for crystalline caesium chloride (p. 389) was described sixteen years ago[3] and was rejected as representative of the halogen compounds of the alkali metals for a number of reasons. Thus, the arrangement in question is a holohedral cubic one and so does not fit the facts; further, in such an arrangement the equilibrium conditions expressed by close-packing will be so delicately balanced that a slight change in their relations, such as would be involved in the passage from caesium chloride to potassium chloride, or rubidium chloride, bromide or iodide, must be expected to involve a change of crystalline form. For these and other reasons we

[1] *J. Chem. Soc.*, **101**, 1902 (1912).

[2] *Ibid.*, **89**, 1683 (1906).

[3] Barlow, *Proc. Roy. Soc. (Dublin)*, **8**, 549 (1897).

gave the preference to the type of arrangement which we ultimately described.[1]

The difficulty suggested by the isomorphous replacement of potassium by ammonium in the sulfate, in which our theory demands the replacement of a potassium atom of volume one, by an ammonium group of volume seven (not nine as stated) elicits the comment (p 394) that "it is hard to see how any sort of analogous symmetry could be constructed in the two cases under these circumstances." We have given an example[2] which indicates how a closely analogous difficulty may be met by our theory in connection with the isomorphism of potassium and ammonium chlorides. We foresee no special difficulty in constructing assemblages, in accordance with our method, which will present geometrical relationships compatible with the isomorphism of potassium and ammonium salts, at the same time we must ask to be judged by what we have already done and not by what still remains for us to do. Moreover, the difficulty which occurs in dealing with the isomorphism of potassium and ammonium does not arise from acceptation of the law of valency volumes and is certainly not surmounted by the view that the potassium atom and the ammonium group occupy approximately the same volume in crystalline potassium and ammonium chloride. The following substances are all alums crystallizing in the cubic system.

K, with $Al(SO_4)_2$ $12H_2O$	Potash alum
NH_4, with $Al(SO_4)_2$ $12H_2O$.	Ammonia alum
NH_3 CH_3, with $Al(SO_4)_2$ $12H_2O$	Methylamine alum
NH_3 C_2H_5, with $Al(SO_4)_3$ $12H_2O$	Ethylamine alum
$NH(CH_3)_2$, with $Al(SO_4)_3$ $12H_2O$	Trimethylamine alum
NH_2 C_5H_{11}, with $Al(SO_4)_2$ $12H_4O$	Amylamine alum
NH_3 C_8H_{18}, with $Al(SO_4)_3$ $12H_2O$.	Coniine alum
$NH(C_7H_7)_3$, with $Al(SO_4)_3$ $12H_2O$	Tribenzylamine alum.

The facts thus tell us that the 44 atoms of the tribenzylamineammonium group can replace the potassium atom in potassium aluminium sulfate without the occurrence of a change in crystalline system; Professor Richards' mode of regarding crystallographic problems makes him confess the difficulty of seeing how any sort of analogous symmetry could survive the replacement of one unit of volume, the potassium atom, by seven units of volume, the ammonium group, in a salt. It can surely not be maintained that cubic symmetry survives the replacement of one potassium atom by 44 other atoms because the 44 occupy the volume originally occupied by the one potassium atom.

The clue to the whole problem here concerned lies, we suggest, in the possibility of homogeneous arrangement of groups or atomic domains of different relative sizes in the same class of crystal symmetry, while, at

[1] *J. Chem. Soc*, **91**, 1179 (1907)

[2] *Ibid.*, **91**, 1204 (1907)

the same time, close dimensional correspondence subsists which is traceable to the operation of the valency volume law.

We may here terminate our present contribution to this discussion, leaving untouched many points which have been raised against us by Professor Richards because they seem to us mainly based on minor misunderstandings of our work. The only one of the conclusions which Professor Richards states in his summary with which we agree is that numbered (3) —"Some facts seem to be quite beyond the reach of their hypothesis "

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

FURTHER REMARKS CONCERNING THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.

BY THEODORE W RICHARDS

Received February 21, 1914

The preceding paper on "The Chemical Significance of Crystalline Form," [1] by Mr. William Barlow and Professor William Jackson Pope, replying to one of mine [2] with the same title, has been submitted to me through the courtesy of the editor of THIS JOURNAL and of the authors of the paper. For this courtesy I am much obliged, and hope that their kind act may be the means of clearing up quickly several misunderstandings which seem to have arisen with regard to the matter in question. Polemics are rarely if ever expedient, but good-natured discussion, either in print or *viva voce*, may serve a useful purpose.

As Messrs. Pope and Barlow infer, I find no fault in the idea of the close-packing of the atoms in crystals. This idea has been, indeed, more or less tacitly assumed in most discussions of the chemical significance of crystalline form. Barlow in his interesting deductive analysis of the geometrical properties of crystalline forms in 1897 begins his final summary with the following sentence: "The main ideas which form the basis of the foregoing inquiry, *viz.*, closest-packing, mutual repulsion of particles, ties, or restraints on this mutual repulsion, are all old conceptions—they have been used by earlier writers and are still adopted by living scientists." [3] Thus we all agree about close-packing. The only difference is as to the

[1] THIS JOURNAL, 36, 1675 (1914).

[2] *Ibid*, 35, 382 (1913)

[3] "A Mechanical Cause of Homogeneity of Structure and Symmetry Geometrically Investigated" (read June 16, received for publication June 18, and published December 20, 1897, appearing as paper lxii in the 8th volume, N. S. of the Scientific Proceedings of the Royal Dublin Society, November, 1898).

Comp. "Molecular Constitution of Matter," by Sir William Thomson, in *Proc. Roy. Soc. of Edinburgh*, 16, 693–715 (1890), quoted by Barlow.

nature and behavior of the entities which are close-packed. This point will be considered shortly.

Again, as the transatlantic investigators rightly point out, the two interpretations with regard to monatomic elements are geometrically in agreement, although the points of view are so divergent. This is not, however, surprising. The nature of the monatomic element admits only of equidistant atomic spacing, and so far as I am aware no other geometric interpretation of the arrangement of a collection of similar spherical atoms has ever been attempted by anyone. In view of this geometrical similarity, Barlow and Pope express their inability to see wherein my view differs from theirs, saying: "We do not know what theory, as distinct from our own, he has in mind." The difference is nevertheless well marked, even in the case of monatomic elements, for although the geometrical arrangement would here be the same according to each theory, the idea of atomic compressibility introduces a factor in the mechanism involving change of volume, which brings this case into line with the more complicated ones soon to be considered. Each side of each atom would be compressed by contact, but each would be equally compressed. When we come to treat of the more complex allotropic forms of elements having polyatomic molecules, the difference between the two points of view stands out in stronger relief. According to the theory of compressible atoms, the affinity which binds the atoms together to make a polyatomic molecule must have a different compressing effect from the cohesion which knits these molecules into the solid condition. Hence equidistant spacing between the atoms in all directions can no longer exist. The difference between my hypothesis and Pope and Barlow's is here, as indeed in the other cases, entirely concerned with the different interpretations as to the results of the action of the forces binding together the atoms in a molecule, and the molecules with one another. In my interpretation I have endeavored to reconcile the crystalline phenomena with other properties of the substances concerned, such as boiling points, melting points, surface tensions, compressibilities, coefficients of expansion, all of which can furnish some clue as to the forces at work; but Pope and Barlow seem to have made no such effort. Their discussion is essentially a geometrical one, and involves the close-packing of *spheres;* whereas my view imagines the "spheres of influence" as much distorted whenever the molecule is composed of more than one atom

As a matter of fact, very little emphasis is placed, in the joint thesis of Barlow and Pope, upon the possible magnitudes of the forces holding the atoms together.[1] In reading the paper one feels that the original tenets of Barlow, as set forth in the earlier paper already referred to, are retained. In this paper (which consists of a highly learned and in-

[1] *J. Chem. Soc.*, **89**, 1676 (1906)

genious deductive analysis of the arrangement of Boscovichian atoms in space), the atoms are often alluded to as mutually repellent (*e. g.*, on pages 529, 547, 580, 675, 686), but little is said about their mutual affinities. Some kind of tie or restraint is presupposed where chemical action is concerned, but the binding together of molecules seems to be of the loosest possible sort. In the papers by the joint authors, no attracting force except gravitation (or its like) seems to have been mentioned; but few chemists would be inclined to admit that gravitation is the only force binding the molecules of solids.

The definite statement is made both in Barlow's early work and in the paper of 1906 (by the joint authors) that the spheres of influence are to be considered as incompressible. To be sure, in this latest paper affirmation is made that they are to be looked upon as incompressible only when no change in pressure is put upon them: " the atomic domains are incompressible because, by definition, no force is operative to compress them;" but according to that definition would not everything be incompressible? Even the most rarefied gas does not change its volume if unacted upon chemically, and if the pressure and temperature remain unchanged. The difference of opinion here seems to be rather one concerning the definition of the word "incompressible," at least as used in the latest paper. The earliest paper by Barlow appears to have used the word in its usual sense.

But entirely apart from any question as to the significance of this term, there is a real and fundamental difference between the two opposing theories. The British investigators enunciated publicly for the first time in 1906 the postulate that the volume which any substance assumes is essentially determined by valency. They contend in their latest paper that this valency volume idea is not an assumption, but a law deduced from the theory of close-packing under the balanced play of centered forces, and that it was obtained as an argued conclusion based upon the interpretation of the facts. Here again one is doubtful as to the definitions which may be given to the terms deduction, hypothesis, theory, and law; but, however these words may be defined, it seems to be perfectly clear that the idea of valency volume is an essential feature in their present quantitative discussion. This is made evident in their definition of equivalence-parameters on page 681 of their paper of 1906. In this paper W signifies the valency volume, and W enters into the value of x; therefore, it also enters into that of y and z, which depend upon x. These values, x, y, and z, are the basis of all their comparisons.

It is this idea of valency volume which I find myself obliged to reject; and the rejection is not by any means based upon minor misunderstandings of the work.

The question at issue seems to be simply as follows: Messrs. Pope and Barlow imagine that their "spheres of influence" of the atoms expand and contract to fit their theory of valency volumes, and this theory has the rigid requirement that in any given compound the volume occupied by an atom is to be assumed as directly proportional to its valency.   No plausible reason why this should be so is given.

On the other hand, the point of view which I am defending maintains that when two atoms are drawn together by a stronger chemical affinity, the volumes of their spheres of influence[1] must be diminished at the surfaces of contact, and that when the molecules are bound together by strong cohesive affinity, their volumes are again diminished by the cohesive pressure exerted upon the contiguous surfaces.   This theory maintains that both affinity and cohesion not only hold the atoms together, but that they *pull* the atoms together.   Hence the volume occupied by a solid or liquid is dependent upon the variable forces which come into play.   The forces are shown to be not arbitrarily determined, but to be inherent in the atoms; and every change in affinity must produce its corresponding change in volume.

These two points of view are perfectly definite and entirely antagonistic. Messrs. Pope and Barlow think that they have obtained support for theirs in some of the facts of crystallography.   In my last paper I endeavored to show, as they state, that all the facts adduced by them are inconclusive, being capable of explanation in other ways.   On the other hand, in support of the opposing theory (which maintains volume to be determined not by an arbitrary choice of valence on the part of the crystallographer, but rather by the actual affinities which play upon the atom), very many facts have been brought forward in my papers upon the significance of changing atomic volume[2] seeming to leave no doubt that solid and liquid volumes are really determined in this way.

Countless facts quoted from these papers might be reviewed to show the reasonableness of ascribing to chemical affinity and cohesion an important share in determining the volume of solids and liquids; for instance, the fact that the less cohesive elements have large molecular volumes and large compressibilities, the fact that, in general, among isomers the more volatile are also the more compressible, less dense, possess less surface tensions and greater coefficients of expansion, the fact that, in general, the exhibition of greater chemical affinity seems to involve greater diminution in volume,

[1] Because these "spheres of influence" always accompany the atoms and seem always to represent them in their volume relations, I call the "spheres" the atoms themselves.   The term "spheres of influence" seems to be unfortunate, because in all compounds these spaces occupied by the atoms can scarcely be spherical; and, moreover, some influences of the atoms unquestionably extend beyond them.

[2] A bibliography of these papers is in THIS JOURNAL, 36, 624 (1914).

all point in one direction.[1] On the other hand, the theory of Messrs.
Barlow and Pope seems to take account of none of these things.

Because of this effect of the powerful forces coming into play, the com-
plete solution of the problem of crystalline form demands many more
far-reaching arguments than ones concerning mere matters of crystallo-
graphic detail.   The knowledge necessary for the satisfactory mathematical
treatment of the subject involves an understanding of the enormous in-
ternal pressures which bind solids together, quite beyond the reach of
any mortal today.   A deductive method is convincing only when all
the factors determining a given phenomenon are taken into account;
and it seems to me that some of the chief factors have been left altogether
out of consideration in the mathematical theory under discussion.   One
is at a loss, for example, as to how the theory of Barlow and Pope can ac-
count for the enormous shrinkage in volume (to much less than half of the
original bulk of the reacting elements) which occurs when caesium com-
bines with liquid chlorine.   The interstices in the most loosely close-
packed system in the original substances (the elements) could not account
for this, because geometrically the cube is less than twice the volume of the
inscribed sphere.   This change of volume is not accidental, and the fact
that the heat evolved and the free energy change exhibited by such changes
show a traceable connection with the work involved in the compression
shows that such volume changes are deeply significant and fundamental.
Atoms cannot be expected to contract and swell up to conform to the ex-
igencies of a deductive geometric theory; their volume-changes must be
expected to be far more logically caused.   ₄

Again, no notice is taken in the immediately preceding paper of a typical
case emphasized in mine, namely, the relation between benzene and tetra-
bromobenzene.   This is not an isolated case, but is typical of a very plenti-
ful class of phenomena, and yet the authors have not attempted to throw
light upon it.   Benzene has a molecular volume of 77.4, tetrabromobenzene
130.2.   They both have the same number of valencies within them, namely,
30, if carbon is considered as a tetrad.   It is evident then that the theory
of Barlow and Pope demands that the carbon should be the same fraction
of the total volume in each case, and the same doctrine holds true with
regard to the two residual atoms of hydrogen.   This involves the assump-
tion that these atoms (or their "spheres of influence") nearly double their
bulk when the other associated atoms are exchanged on a purely univa-
lent basis.   No reason whatever for this extraordinary increase in volume
has been assigned, and I cannot help thinking that any chemist who has
seriously considered the subject of molecular volume will agree with me
in thinking that the Pope-Barlow assumption is irreconcilable with the

[1] "The Faraday Lectures 1911," *J. Chem. Soc.*, **99**, 1201 (1911); *Science N. S.*,
34, 537 (1911).

phenomena. The more reasonable explanation is that the atomic volume of bromine in combination is much larger than that of hydrogen, as all of the well-known considerations of Kopp indicate. Let me emphasize once more the fact that this is a typical case, and that it was advanced in my previous paper as a direct challenge. The fact that it was ignored seems to imply that it could not be answered.

Since some of the other objections raised in my previous paper seem to have been misunderstood, the more important differences of opinion about them may be briefly reviewed. For example, with regard to the results of Le Bas, the eminent controversialists seem to have overlooked the fact that while I explicitly referred to the obviously closer agreement of their calculated figures as compared with those corresponding to my assumption, I pointed out that even the most divergent results fit the facts quite as closely as anyone has a right to expect, because of the arbitrary assumption as to the temperature of comparison   Barlow and Pope chose the ratio: volume H = $1/4$ volume carbon (exactly), and in order to show that the deviations produced even by a great departure from this proportion were unimportant, I chose the entirely different ratio· volume of hydrogen = $1/2$ volume of carbon. It is easy for anyone to calculate, however, that if such a ratio as 1   3.5 or 1   4 5 or e   n 1 . 5 is chosen, results of the same order of accuracy as those obtained from Barlow and Pope's exact ratio 1 . 4 are obtained; for example, if hydrogen is taken as 2.553 cc. and carbon is taken as 12.765 cc (five times the hydrogen) the theoretical values calculated for the first fifteen hydrocarbons in the table of Le Bas agree on the average at least twice as well with the observed facts as those computed according to Barlow and Pope's assumption of the ratio 1 : 4.[1]

TABLE GIVING TYPICAL COMPARISONS OF HYDROCARBONS WITH LESS THAN 30 ATOMS OF CARBON

	Mol vol at melting point Found	Barlow and Pope's assumption Vol C = 4 Vol H	Error	New assumption Vol C = 5 Vol H	Error
$C_{11}H_{24}$ ..	201 4	202 0	0 6	201 7	0 3
$C_{12}H_{28}$	237 3	237 6	0 3	237 4	0 1
$C_{14}H_{33}$	273 2	273 2	0	273 2	0
$C_{16}H_{17}$.	326 9	326 7	0 2	326 8	0 1
$C_{22}H_{44}$.	398 3	398 0	0 3	398 3	0
$C_{27}H_{56}$ ..	487 4	481 1	0 3	487 6	0 2

How, therefore, they can claim that these figures afford any significant support for any exact ratio, I do not understand.   To me it seems that their argument amounts to a process which might be called mathematical hair-splitting, especially when the quality of the data in question is taken

[1] The last three with over thirty atoms of carbon to the molecule are not quite so conformant, but, even as a whole, the series of calculated results is about as good as Pope and Barlow's.

into consideration. Moreover, the paraffin hydrocarbons were liquids, not crystals, at the temperatures measured; and in any case, they are unique in their properties, hence it is not safe to transfer conclusions drawn from them to other compounds.[1] The principles used by Le Bas and Barlow and Pope, if applied to aromatic hydrocarbons, completely collapse. In the light of these remarks, a careful perusal of my earlier statements upon page 385 will furnish evidence which needs no further elucidation. I beg leave to dissent entirely from their statement with regard to this matter on page 1681 of their paper.

The immediately foregoing paper contains several examples brought forward in order to show that the theory of Barlow and Pope is capable of showing resemblances between morphotropic organic and inorganic substances. It seems to me that these examples add little to the general argument; they are really of the same class as the partial symmetries of organic substances discussed in my earlier paper. The bringing forward of these examples seems rather to indicate a misunderstanding as to the general criticism of the method. I have from the first admitted cordially that the mathematical method of equivalence-parameters involving valency volume is capable of showing resemblances; the difficulty with it is rather that it seems to be capable of showing resemblances where none exist, and, therefore, its results must be received with great caution.

In a number of minor points also there seems to be misconception or misunderstanding. For example, Mr. Barlow and Professor Pope must adopt some other structural formula for ammonium chloride than that which corresponds with my notion. They often arbitrarily choose, in assigning their valency volume, the lowest valency which an element exhibits, regardless of the actual valency in the particular case. For example the radical of ammonium is supposed to have seven valencies in all; $NH_4 + H_2$ seems to be considered as a univalent complex. But is not this (like a number of their other methods) rather an arbitrary proceeding? To me NH_4Cl seems to have ten valencies, five on the nitrogen, one on each hydrogen, and one on the chlorine. Therefore, if each valency had an equal volume, nine volumes would belong to ammonium and one to chlorine. Again, the intimate structure of the cube of caesium chloride, as illustrated in my previous paper, must certainly be considered as hemihedral, because both the chlorine atoms and the caesium atoms are arranged in tetrahedral symmetry.[2] The fact that externally the form is cubic, makes the structure holohedral only from a superficial geometric point of view. The question here is, of course, entirely as to the significance attached to the words hemihedral and holohedral, which in this case would differ according as the surface of the crystal or its ultimate structure is

[1] L. J. Henderson, "The Fitness of the Environment," p. 215 (Macmillan), (1913).
[2] See Barlow, Loc. cit., p. 550.

taken into consideration. That Barlow, in 1897, proposed and rejected something analogous to the arrangement which I pictured was overlooked by me, because his diagram is so very different in appearance (*loc. cit.*, p. 550), but the fact does not change my opinion that the aforesaid picture is the most reasonable explanation of the facts. If the atom is acknowledged to be compressible, this arrangement is as closely-packed as any other, and it would be firmly tied together by the strongly attractive affinity of the two components, thus forming a thoroughly stable system. The substitution of potassium for some of the caesium would not be difficult in a compressible system. Incidentally, the introduction of this question gives me the opportunity of acknowledging that Professor Sollas in a very interesting paper published in the Proceedings of the Royal Society in 1898,[1] proposed a structure of sodium chloride essentially similar to that advocated by me for caesium chloride, without, however, the addition of the idea of atomic compressibility. Sollas's theory with regard to this substance seems to me far more reasonable than that of his antagonists, but his concepts are less satisfactory when they depart from the idea of close-packing.

It would be wearisome to consider here every detail of the misunderstanding involved in the paper of Mr. Barlow and Professor Pope; indeed, this is not necessary, for a careful perusal of the papers in question will give the intelligent reader abundant opportunity to decide between the alternatives according to his appreciation of the cogency of the respective arguments. It is important to note that no evidence in any way contrary to the theory of compressible atoms has been adduced by the eminent transatlantic investigators.

Nevertheless one further point introduced by their paper seems worthy of further discussion, especially since it concerns the general principles of research. The authors feel that a qualitative argument must necessarily give way before a highly developed quantitative one; and because this feeling seems to be general with regard to many physicochemical phenomena, I am glad to take this opportunity to express my attitude. No one could believe more completely than I in the importance of quantitative mathematical discussion; I have given most of my life to the attempt to secure more accurate quantitative data of many kinds. A scientific argument which is wholly lacking in quantitative support cannot be satisfactory; but on the other hand a highly developed mathematical treatment which rests upon unsound premises is usually much worse than none. Such a treatment is likely to carry with it a false feeling of security, and to be less valuable than a merely qualitative discussion based upon sound premises. To cite an extreme example, the qualitative discussion of the nature of oxygen by Rey, Hooke, and Mayow in the seven-

[1] W. J. Sollas, *Proc. Roy. Soc.*, **63**, 273 (1898).

teenth century was much more nearly correct than the later quantitative explanation of the ultra-phlogistonists, which ascribed negative gravity to phlogiston in order to explain many of the same facts. The latter explanation appeared to be at least consistent from a quantitative point of view, but was very ill-founded as regards its fundamental premises. Not only in this matter of crystalline form, but in many other physico-chemical problems, it seems to me highly desirable that the fundamental premises or original assumptions should be reasonable, and in accordance with as wide a variety of facts as possible, even if the resulting system appears to us now to be too complex to receive complete mathematical treatment.

Besides, the fact should be emphasized that my views concerning the significance of changing atomic volume by no means rest upon a mere qualitative basis; they are supported by many observations of a highly quantitative nature.

To sum up the situation, it seems to me that the immediately preceding paper under discussion has not attempted to answer some of the most important objections to the deductive theory; that the authors have misunderstood others; that they adopt a mathematical treatment which tends often to make disagreeing results more harmonious, and then find crystallographic confirmations of their deductive tenets which do not seem to me to be cogent; that here as before they seem to have essentially overlooked the very large internal pressures which must exist in solids, and have not heeded the arguments from which the existence and effects of these pressures are inferred; that the paper gives evidence of an illusory security sometimes felt by those who put their trust in a complex mathematical superstructure rather than in a firm foundation of sound assumptions, and that no argument has been advanced to show that my fundamental assumptions are not sounder than those of the joint authors. On the other hand, the various papers on the significance of atomic volume have brought forward so many evidences in favor of atomic compressibility as to put the burden of proof on any contrary hypothesis.

In conclusion it gives me much pleasure to express once more my appreciation of the real service which Mr. Barlow and Professor Pope have done by collating a great quantity of crystallographic data; and to this expression I must add my regret that I have found their fundamental doctrine of valency volume irreconcilable with a broader view of the nature of solids and liquids and the mechanism of chemical change.

HARVARD UNIVERSITY, CAMBRIDGE, MASS

Additional Note by William Barlow and William Jackson Pope.

The perusal of the two foregoing communications will probably convince the reader that little of public utility will result from the further

continuance of the discussion in THIS JOURNAL. This reason alone would lead us to decline further controversy on the subject for the present after having had the opportunity of putting our case forward in these pages; another and weightier reason seems now, however, to render further immediate discussion superfluous. During the last year or two a method for the practical determination of crystal structure has been developed by Laue and by W. H. and W. L. Bragg, which gives every promise of ultimately leading to very precise information concerning the arrangement of the atoms in a crystalline structure. While we greatly appreciate the frank and courteous manner in which Professor Richards has dealt with our crystallographic work we think that further discussion on the lines laid down in the preceding two papers may well be postponed until the important developments which are promised have had time to mature

CAMBRIDGE, ENGLAND

THE MIXED CRYSTALS OF AMMONIUM CHLORIDE WITH MANGANESE CHLORIDE.

BY H W. FOOTE AND BLAIR SAXTON

The products which form when mixed solutions of ammonium and manganese chlorides are allowed to crystallize, have been investigated repeatedly and a number of double salts have been described by different investigators.[1] In the early work, the possibility of mixed-crystal formation was not taken into account, so that any material which appeared homogeneous was considered a chemical compound and at least four double salts were described which undoubtedly do not exist. Lehman[2] first recognized that ammonium chloride was capable of forming a curious type of mixed crystal or solid solution with manganese chloride, as well as with a number of chlorides of other metals such as nickel and ferrous and ferric iron, and he and also Johnsen[3] investigated them, chiefly from a crystallographic standpoint. The most complete investigation on the double salts of the chlorides of ammonium and manganese was carried out by Saunders.[4] He repeated the work of some of the previous investigators, following their directions so far as practicable and concluded that only one double salt forms, which has the formula $2NH_4Cl.MnCl_2.-2H_2O$. He analyzed a number of products which did not give rational formulas, and concluded that these were mechanical mixtures; but he did not consider the possibility of true mixed-crystal formation. Lehman's work, which appeared nine years previously, was apparently un-

[1] A summary of the literature on the subject will be found in Abegg's "Handb. der anorg. Chem ," 7th Group, p. 705.

[2] Z. Kryst., 8, 438 (1883).

[3] N. Jahrb. Min., 2, 93 (1903).

[4] Am. Chem. J., 14, 127 (1892).

known to Saunders. The extent of mixed-crystal formation and the conditions which produce mixed crystals instead of double salts have not been determined. While investigating these points, some interesting, and rather unusual, relations have been discovered. Our results show that ammonium chloride and the double salt form two series of mixed crystals, there being a gap between the limiting composition of each type. From the results, conclusions can be drawn as to the components making up the mixed crystals, which has not been possible before.

The method which has been used to determine the solid phases and the conditions for their formation, is essentially the same solubility method that has been used before, by one of us,[1] in determining the mixed crystals of ammonium chloride with nickel and cobalt chlorides. The solubility of varying mixtures of ammonium and manganese chlorides has been determined at 25°, analyzing both residues and solutions. From a series of such results, the solid phases which form can be determined.

Weighed quantities of the recrystallized salts were transferred to bottles, treated with water and warmed till all dissolved. The bottles were rotated for at least 48 hrs. in a thermostat at 25°, using glass rods in the bottles to assist in reaching equilibrium. After the residues had settled in the bottles, weighed portions of solution were drawn off through a filter of glass wool for analysis. The residues were then removed and dried as rapidly as possible between filter papers. Ammonia was determined in the usual manner, by distilling with potassium hydroxide, absorbing the ammonia in standard acid and titrating the excess. Manganese was precipitated as NH_4MnPO_4, filtered on a Gooch crucible and weighed as $Mn_2P_2O_7$. Water was calculated in the residues from the percentage of manganese chloride, assuming that the latter was present as dihydrate. The results for water are practically the same that would be obtained by difference. The analytical data for solutions are undoubtedly somewhat more accurate than for residues. This is because the solution can be obtained free from residue, while the latter is of necessity somewhat contaminated with solution.

The results obtained are given in Table I.

The results are shown graphically in Fig. 1. The percentage of ammonium chloride in the residue is plotted as abscissa and the composition of the solution as ordinate. Two curves are shown, one expressing the composition of the solutions in percentage of ammonium chloride, the other, in percentage of manganese chloride.

Nos. 1–5 in Table I show variable composition of residue and of solution. They are represented in Fig. 1 on the curves AB and CD. In this series, it is evident that mixed crystals of ammonium chloride with varying amounts of manganese chloride dihydrate were present. They correspond

[1] This Journal, **34**, 880 (1912).

TABLE I —SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND MANGANESE CHLORIDE AT 25°

	Solution		Residue				
No	% NH$_4$Cl	% MnCl$_2$	% NH$_4$Cl	% MnCl$_2$	% H$_2$O	Total	Residue contains
1	23 97	7 97	93 83	5 31	1 52	100 66	
2	22 94	9 65	90 24	7 76	2 22	100 22	
3	21 45	12 31	83 98	12 41	3 55	99 94	α mixed crystals
4	21 18	13 38	82 03	14 31	4 09	100 43	
5	20 10	15 19	76 20	18 60	5 32	100 12	
6	19 70	15 92	74 27	20 03	5 73	100 03	
7	19 75	16 02	72 74	21 58	6 17	100 49	α and β mixed
8	19 69	16 05	70 41	22 93	6 56	99 90	crystals
9	19 67	15 47	63 85	28 32	8 11	100 28	
10	17 09	18 76	56 18	34 40	9 84	100 42	
11	15 05	22 44	47 06	41 33	11 83	100 22	β mixed crys-
12	13 17	24 52	42 81	44 87	12 84	100 52	tals or double
13	9 15	29 24	39 36	47 64	13 63	100 63	salt, 2NH$_4$Cl -
14	5 90	34 78	37 76	48 79	13 96	100 51	MnCl$_2$ 2H$_2$O
15	3 77	39 48	35 66	50 00	14 31	99 97	
16	2 98	43 71	16 29	58 27			Double salt and
17	2 94	43 44	7 30	61 88			manganese chlo-ride

to the mixed crystals with ferric chloride investigated by Roozeboom,[1] van der Kolk[2] and Mohr,[3] and with nickel and cobalt chlorides investigated by one of us [4] We shall call these crystals the α variety Nos 10–15 again show variable composition of residue and solution They are represented in Fig 1 on the curves EF and GH It will be noted, however, that the curves are nearly vertical toward the end, which means that the composition of the residue is nearly constant but has variable solubility This shows the presence of a double salt The double salt described by Saunders contains 39 8% NH$_4$Cl, which is nearly the same as the residue of No 13, lying on that part of the curve which is nearly vertical Nos 14 and 15 contain somewhat more manganese and less ammonium chloride than does the pure double salt It must be remembered, however, that the residues in determining solubility were of necessity very finely divided, in order to insure equilibrium with the solution, and were, therefore, somewhat contaminated with mother liquor This accounts for the variation in composition There seems, therefore, no doubt that the 2 1 double salt exists This series of results, however, gives residues containing up to 64% of ammonium chloride, or about 24% more than the pure double salt, showing that the latter forms a

[1] Z physik Chem , 10, 145 (1892)
[2] Ibid , 11, 167 (1893)
[3] Ibid , 27, 193 (1898)
[4] THIS JOURNAL, 34, 880 (1912)

series of mixed crystals containing an excess of ammonium chloride. These we have called β crystals. Before the solubility series was completed, there appeared to be a complete series of mixed crystals between ammonium chloride and the double salt. Nos. 6–9 in Table I, represented in the figure by the horizontals, have, however, practically constant
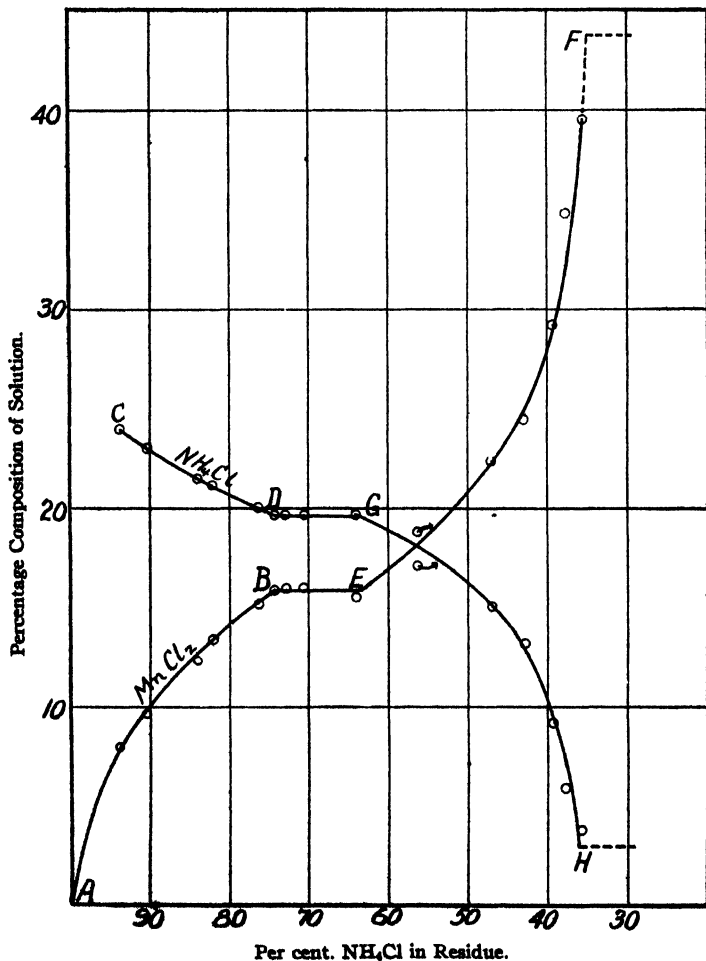
solubility with variable residue, showing that two solid phases were present. In this series, the α and β crystals were evidently both present in variable proportions.

To obtain the pure double salt in well crystallized condition, we pre-

pared a solution whose composition was calculated from our solubility data, such that after 10% of the dissolved salts had crystallized, the remaining solution would have approximately the composition of the solution in No. 13. The amounts used were 52 g. NH_4Cl, 233 g $MnCl_2$.-$4H_2O$; and 204 cc. H_2O. The salt separated in good crystals, similar to those obtained by Saunders. It should be mentioned in this connection, that, where either form of mixed crystal was obtained, the material was in a fine granular, poorly crystallized condition, even when it separated slowly from a considerable volume. An analysis of the salt gave the following results·

	I	II	Calculated for $2NH_4Cl\ MnCl_2\ 2H_2O$
NH_4Cl	40 01	40 05	39 80
$MnCl_2$	47 21	46 96	46 81

Another crop of crystals was obtained from a solution which corresponded in composition with that of No. 14 in Table I. The analysis of this crop of crystals was as follows

	I	II
NH_4Cl	39 00	38 99
$MnCl_2$	47 47	47 59

The large excess of manganese chloride in the solution caused some contamination, but the results are sufficiently close to the theory for double salt to prove that it was present.

The results which have been given show that a very rare type of solid solution exists in the present case, in which a single salt and a double salt are each capable of taking up very considerable quantities of the other to form homogeneous mixed crystals. The case is somewhat similar in character to the isomorphism between dolomite and calcite.[1] Nos. 6 and 9 in Table I show the approximate limits in composition of the α and β crystals at 25°.

Calorimetric Results.

In connection with the work on solubility, we have carried out a series of calorimetric determinations which show the heat effect of solid solution. These results confirm the existence of the two types of crystals and also offer very strong evidence regarding the components which make up the mixed crystals.

The method adopted was as follows The heat of solution of 10 g. of mixed crystals in 500 g. of water was determined. This determination was duplicated in every way except that an equal weight of a mechanical mixture of ammonium chloride and manganese chloride dihydrate was substituted for the mixed crystals. The difference gives the heat involved in the formation of the mixed crystals from the single salts. From these determinations, results which are comparable in different lots of mixed

[1] *Am. J Sci.*, **37,** 339 (1914).

crystals may readily be calculated. The calorimeter used in the work has been described by Haigh.[1] The silver containing-vessel held about 500 cc. The thermometer used was corrected by comparison with a standard instrument. The total heat capacity of the calorimeter, using 500 g. of water in all the work, was 513.7 calories. The salts were finely ground in every case and dissolved so rapidly that thermometer readings could be taken after an interval of two minutes. The temperature of the water in the outer jacket and in the silver vessel, and the rate of stirring, were so adjusted that radiation corrections were minimized.

For the mechanical mixtures, it was necessary to prepare the dihydrate of manganese chloride, since both the double salt and the mixed crystals contain this component. The method used is that given by Lescoeur[2] and by Dawson and Williams.[3] The method consists essentially in dissolving the tetrahydrate in 95% alcohol and saturating the solution with hydrochloric acid gas. For our purposes, 200 g. of the salt were dissolved in 350 cc. of alcohol. The first yield was about 100 g. of the salt, but more separated later after standing. The product obtained is exceedingly pure. It was dried in a desiccator over caustic potash and finally heated in an air bath at 50° to remove traces of alcohol and acid. To test the purity, manganese was determined as sulfate:

<p style="text-align:center">MnCl$_2$ found: 77.66, 77.72; calc. 77.74.</p>

Four samples of mixed crystals were prepared. Two of these were the β crystals, one was the α form and the other (No. 2) prepared before we were aware that two forms existed, was nearly pure α, with probably a slight admixture of the β form. The composition of the solutions from which the samples crystallized was calculated from solubility data, allowing about 10% of the salts dissolved to crystallize. The crystals were small and opaque. Those belonging to the β type had a marked pink color, while the others, with more ammonium chloride, were more nearly white. The following results were obtained by the analysis of each crop.

	NH$_4$Cl, %.	MnCl$_2$, %.	H$_2$O, %. (Calculated as dihydrate.)	Total.	Type of crystals.
1	78.55	16 99	4.80	100.34	α
2	75.00	19.78	5.53	100.31	α[4]
3	61.25	29.55	8.46	99.26	β
4	47.96	40.51	11.59	100.06	β

The above results represent, of course, the average composition of each sample. Undoubtedly the first crystals deposited from solution contained somewhat more ammonium chloride. The percentages given were re-

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[1] This Journal, 34, 1144 (1912).

[2] Ann. chim. phys., [7] 2, 78 (1894).

[3] Z. physik. Chem., 31, 59 (1899).

[4] Probably contained a small amount of β.

calculated to an even 100% when mechanical mixtures were to be made of the same composition.

The following calorimetric results were obtained, using the mixed crystals whose composition is given above, and mechanical mixtures of the same composition (Tables II–V). The heat capacity of the calorimeter and water, was in all cases 513.7 calories.

TABLE II.

α Mixed Crystals, 78.38% NH₄Cl.

	$t_2 - t_1$.	Heat effect (in calories).	Average heat effect (in calories).
1. Mechan. mixture..............	—0.841	—432.1	—432.6
2. Mechan. mixture..............	—0.843	—433.1	
3. Mixed crystals................	—0.815	—418.7	—419.5
4. Mixed crystals................	—0.818	—420.2	

TABLE III.

α Mixed Crystals (chiefly).   74.69% NH₄Cl.

1. Mechan. mixture..............	—0.771	—396.1	—394.8
2. Mechan. mixture......	—0.766	—393.5	
3. Mixed crystals................	—0.755	—387.9	—389.4
4. Mixed crystals................	—0.761	—390.9	

TABLE IV.

β Mixed Crystals.   61.99% NH₄Cl.

1. Mechan. mixture..............	—0.472	—242.5	—240.6
2. Mechan. mixture..............	—0.467	—239.9	
3. Mechan. mixture...........	—0.466	—239.4	
4. Mixed crystals...	—0.537	—275.9	—274.9
5. Mixed crystals..............	—0.533	—273.8	

TABLE V.

β Mixed Crystals.   47.96% NH₄Cl.

1. Mechan. mixture..............	—0.167	— 85.8	— 83.6
2. Mechan. mixture..............	—0.161	— 82.7	
3. Mechan. mixture..............	—0.160	— 82.2	
4 Mixed crystals................	—0.241	—123.8	—121.8
5. Mixed crystals................	—0.233	—119.7	

The actual heat effect caused by the formation of 10 g. of mixed crystals from the single salts is obviously equal to the heat of solution of the mechanical mixture minus that of the mixed crystals. These values are given in Table VI.

TABLE VI.

Heat of Formation of 10.00 g. Mixed Crystals from the Single Salts.

	NH₄Cl in salt. %.	Type of crystal.	Heat effect (in calories).
1...............	78.38	α	—13.1
2...............	74.69	α (chiefly)	— 5.4
3...............	61.99	β	+34.3
4...............	47.96	β	+38.2

There are two conclusions to be drawn from these results without recalculating them in any manner. The heats of formation are small compared with the heats of solution of the salts in water and the heat of formation of the β crystals is positive while that of the α crystals is negative. The small heat of formation is perhaps to be expected, as the few values which have previously been determined on the heat of formation of mixed crystals have all been small. The positive and negative heats of formation offer further evidence that the α and β crystals are of different type.

To recalculate the above results on a gram molecular basis, brings up the question of what components are to be considered in the mixed crystals. The β crystals can hardly be considered otherwise than a solid solution of ammonium chloride in the double salt, but it is evident that the α crystals may be considered as a solid solution, either of the double salt, or of manganese chloride dihydrate, in ammonium chloride. Any thermal calculation based on the double salt requires its heat of formation from the single salts. This has been determined by the method given above, using, as before, 10 g. of material in each determination.

The results obtained are in Table VII.

TABLE VII.—HEAT OF FORMATION OF DOUBLE SALT $2NH_4Cl.MnCl_2.2H_2O$ FROM NH_4Cl AND $MnCl_2.2H_2O$.

	t_2-t_1.	Heat effect (in calories)	Average heat effect.	Molecular heat of formation of double salt.
1. Mechan. mixture.........	+0.025	+12.8		
2. Mechan. mixture.........	+0.033	+17.0	+15.8	
3. Mechan. mixture.........	+0 034	+17 5		
				+1084 calories
4. Double salt......... ...	—0.051	—26.2		
5. Double salt..............	—0.046	—23.6	—24.5	
6. Double salt..............	—0.046	—23.6		

From the data we have calculated the heat of combination of 1 gram molecule of double salt with ammonium chloride in the α crystals and of 1 gram molecule of ammonium chloride with the double salt in the β crystals. The results are given in Tables IX and X.

TABLE IX.—HEAT OF COMBINATION OF 1 MOL DOUBLE SALT WITH AMMONIUM CHLORIDE (α CRYSTALS).

	Total per cent. NH_4Cl in mixed crystals.	Mols NH_4Cl: 1 mol double salt.	Heat of combination.
1.......... .	78.38	8.97	—2067
2............	74.69	6.93	—1427

TABLE X.—HEAT OF COMBINATION OF 1 MOL AMMONIUM CHLORIDE WITH DOUBLE SALT (β CRYSTALS).

	Total per cent. NH_4Cl in mixed crystals.	Mols double salt: 1 mol double salt.	Heat of combination.
3..	61.99	0.34	+129
4...	47.96	1.26	+133

No. 2 is probably the least accurate, for reasons previously given, and the result is low. Nos. 3 and 4 show nearly constant heat of combination.

In Table XI the thermal results are recalculated to show the heat of combination, assuming that the mixed crystals are merely solid solutions of $MnCl_2.2H_2O$ in ammonium chloride.

TABLE XI —HEAT OF COMBINATION OF I MOL $MnCl_2 2H_2O$ WITH NH_4Cl.

	Per cent. NH_4Cl in mixed crystals	Heat effect Cals
1	78 38	— 981
2	74 69	— 345
3 ·	61 99	+1461
4	47 96	+1189

The results given in Tables IX–XI throw some light on the question which has often been discussed, as to how these mixed crystals, and others of similar type, are to be regarded. Previously, only the α type of crystals has been investigated and there has been no means of deciding whether the component in solid solution was the chloride of the polyvalent metal or a double salt of the latter with ammonium chloride. Without means of deciding, the simplest method of representing the facts has been to regard the crystals as solid solutions of the single salt in ammonium chloride. The heats of combination or solid solution given in Tables IX and X, assuming that the components are ammonium chloride and double salt, are at least approximately constant for each type of crystal, a regularity which is comparable with the nearly constant heat of solution of a salt in water with varying dilution. As will be shown in the article which follows, the heat of solid solution in a simple case of isomorphism is also very nearly constant, independent of dilution. Assuming that mixed crystals of ammonium chloride and manganese chloride form, Table XI, there is no constancy or regularity evident. The evidence, it seems to us, shows that the double salt is present in both types of mixed crystals. The fact also that the double salt can take up ammonium chloride (β crystals) makes it fair to assume that the reciprocal relation exists of the double salt in ammonium chloride (α crystals).

The α crystals are similar in solubility relations to the mixed crystals with nickel and cobalt chlorides, although no corresponding double salts form in pure condition. These should undoubtedly be 'regarded as belonging to the same type, containing the unstable double salts $2NH_4Cl.-NiCl_2.2H_2O$ or $2NH_4Cl.CoCl_2.2H_2O$ in ammonium chloride.

It may be worth while to point out that there are other cases of solid solution between dissimilar substances, where there is uncertainty as to the components. For instance, pyrrhotite may be regarded as a solid solution of pyrite or of sulfur in ferrous sulfide; a hardened steel may be considered as a solid solution of iron carbide or of carbon in iron, and nephelite, as it occurs in nature, as a solid solution of albite or of silica in the compound $NaAlSiO_4$. Analogy with the case investigated suggests

that the components in these instances are iron sulfide and pyrite, iron and iron carbide and nephelite and albite. Further investigation is needed, however, to decide these points.

SHEFFIELD CHEMICAL LABORATORY,
YALE UNIVERSITY, NEW HAVEN, CONN.

ON THE HEAT OF FORMATION OF SOLID SOLUTIONS.

BY H. W. FOOTE AND BLAIR SAXTON.

Ever since van't Hoff pointed out that isomorphous mixtures could be considered as solid solutions, the problem has been an interesting one as to what extent the properties of such mixtures are a linear function of composition.   It is safe to say that, in general, the properties are much more nearly linear than are the properties of liquid solutions.   For instance, probably no isomorphous mixtures diverge as widely in properties from a linear relation as solutions of water and nitric acid.   This is because substances which are isomorphous are usually very closely related chemically, while liquids which are totally unrelated may dissolve each other readily.   Some properties are so nearly linear that it has not been possible to measure any difference.   Retgers has shown, for example, that the specific gravity of isomorphous mixtures is in general what would be calculated if they were considered as mechanical mixtures.   This property, however, cannot be measured with very great accuracy and it is probable that a difference does exist but that it is small.   Melting points and vapor pressures, so far as they are known, commonly show small variations from the linear relation.   These small variations in properties are an expression of the fact that isomorphous mixtures contain a somewhat different amount of energy than mechanical mixtures of the same composition do and that isomorphous mixtures have what may be termed a heat of solid solution which, in general, is small.   Ostwald[1] demonstrated this in a few cases before van't Hoff's work appeared, and the same has been shown since, notably by Sommerfeldt,[2] Beketoff,[3] Kurnakov and Zemcynznyj[4] and Wrzesnewski.[5]   The results all show that there is a small positive or negative heat of formation.

Salts which are isomorphous with each other only to a limited extent are in some ways comparable with partially miscible liquids.   The composition of each solid, when it has become saturated with the other, is a function of the temperature, as it is with liquids.   With liquids, however,

[1] J. prakt. Chem., 25, 1 (1884).
[2] Jahrb. Mineral., Beibl., 13, 435 (1899–1901).
[3] Z. anorg. Chem., 40, 355 (1904).
[4] Ibid., 52, 186 (1907).
[5] J. Russ. Phys. Chem. Soc., 43, 1364 (1911).

temperature usually, though not always, affects the solubility of each one in the other in the same way. Thus, rising temperature increases the solubility of aniline in water and of water in aniline. With solids, so far as we are aware, a change in temperature has opposite effects on the solubility of each solid in the other. For instance, silver and sodium chlorates each form a limited series of mixed crystals with the other.[1] As the temperature rises, the amount of sodium chlorate which silver chlorate can take up, forming tetragonal crystals, falls off, while the amount of silver chlorate increases which is taken up by sodium chlorate to form cubes. It appears from the principle of Le Chatelier that there should be a connection between the heat of solid solution and change in the mixing limits with temperature. Since the solubility of sodium chlorate in silver chlorate decreases as the temperature rises, the heat of solid solution should be positive while the reverse should hold for the other type of mixed crystals. Strictly, this would be true for the heat of solid solution only when the crystals are near their mixing limit, but there is evidence that this value does not change greatly with dilution.

In the present article, we shall give the results of an experimental determination of the heats of solid solution of sodium chlorate in silver chlorate and of silver chlorate in sodium chlorate. The same method has been used in obtaining the heats of solid solution that other investigators have used for a similar purpose. It consists essentially in determining the heats of solution in water of the mixed crystals and of mechanical mixtures having the same empirical composition. The heat of solution of the mechanical mixture minus that of the mixed crystals gives the heat of formation of the latter from the single salts.

The silver chlorate used in this work was prepared by treating precipitated silver carbonate in excess with a solution of chloric acid, filtering and evaporating to crystallization. It was recrystallized before use. The chloric acid required in making this salt was prepared by treating a solution of pure barium chlorate with a calculated amount of sulfuric acid. The solution gave no test for either barium or sulfuric acid. Sodium chlorate was prepared by recrystallizing the commercial product.

Four samples of mixed crystals were prepared, using the data given by Foote[2] as a guide in making up the solutions. Two of the samples were on the sodium chlorate side and crystallized as cubes. The others contained an excess of silver chlorate and were tetragonal. In their analysis, silver was determined as chloride and calculated to chlorate. Sodium chlorate was determined by difference. Following are the analyses of the four samples used:

[1] Foote, *Am. Chem. J.*, **27**, 345 (1902).
[2] *Loc. cit.*

		AgClO₃. %	NaClO₃. %
1.	Isometric....	15.02	84.98
2.	Isometric. .	30 31	69.69
3.	Tetrahedral.	63 79	36 21
4.	Tetrahedral	73 84	26.16

All samples were finely ground and sifted before use. It was necessary to use bolting cloth in place of a metal sieve when silver chlorate was present

The calorimeter was the one mentioned in the preceding article, and was described by Haigh.[1] The stirrer was made of glass instead of brass to prevent a reaction with the solution. The greatest care was taken to make the conditions in the different determinations as nearly alike as possible The rate of stirring and the temperature of the water in containing vessel and outer jacket were so regulated that radiation corrections were minimized The results obtained are given in Tables I–IV.

TABLE I —SILVER CHLORATE IN SODIUM CHLORATE

15 02% AgClO₃   Isometric mixed crystals

Material	Weight g	t_2-t_1	Heat capacity of calorimeter	Heat effect	Average heat effect (Calories)
Mechan mixture	10 00	—0 929°	513 7	—477 3	
Mechan mixture	10 00	—0 932	513 7	—478 8	. —478 1 cal
Mixed crystals	10 00	—0 916	513 7	—470 6	
Mixed crystals .	10 00	—0 914	513 7	—469 5	—470 1

TABLE II —SILVER CHLORATE IN SODIUM CHLORATE.

30 31% AgClO₃   Isometric mixed crystals

Mechan. mixture	10 00	—0 893	515 6	—460 4	
Mechan mixture	10 00	—0 896	514 6	—461 1	
Mechan. mixture............	10.00	—0.902	514.6	—464.1	—462.2
Mechan. mixture............	10 00	—0.900	514.6	—463.1	
Mixed crystals..............	10.00	—0.872	515.6	—449.6	
Mixed crystals..............	10.00	—0.871	515.6	—449.1	—449.4

TABLE III.—SODIUM CHLORATE IN SILVER CHLORATE.

63 79% AgClO₃.   Tetragonal mixed crystals.

Mechan. mixture............	10.00	—0.829°	515.6	—427.4	
Mechan. mixture............	10.00	—0.835	515.6	—430.5	—429.3
Mechan. mixture............	10.00	—0.834	515.6	—430.0	
Mixed crystals..............	10.00	—0.886	515.6	—456.8	
Mixed crystals.......:......	10.00	—0.886	515.6	—456.8	—456.8

[1] THIS JOURNAL, 34, 1144 (1912).

TABLE IV.—SODIUM CHLORATE IN SILVER CHLORATE.
73.84% AgClO₃. Tetragonal mixed crystals.

Material.	Weight.	$t_2 - t_1$.	Heat capacity of calorimeter.	Heat effect.	Average heat effect. (Calories.)
Mechan. mixture............	10.00	—0.818°	514.6	—420.9	
Mechan. mixture............	10.00	—0.813	514.6	—418.3	
Mechan. mixture............	10.00	—0.818	514.6	—420.9	
Mechan. mixture............	10.00	—0.829	514.6	—426.6	—422.8
Mechan. mixture............	10.00	—0.823	514.6	—423.5	
Mechan. mixture......... ..	10.00	—0.829	514.6	—426.6	
Mixed crystals..............	10.00	—0.859	514.6	—442.0	—441.5
Mixed crystals..............	10.00	—0.857	514.6	—440.9	

From the results given above, we have calculated the heat effect due to the formation of a solid solution by one mol of solute (Table V).

TABLE V.—MOLECULAR HEAT OF SOLUTION.

No	Type of crystals.	Mols solvent· 1 mol solute.	Heat effect of 10 g.	Molecular heat of solution. (Calories.)
1.	Isometric.........	10.17 NaClO₃	— 8 0	—1019 (AgClO₃)
2.	Isometric...........	4.13 NaClO₃	—12.8	—1017 (AgClO₃)
3.	Tetragonal..... ...	0.98 AgClO₃	+27.5	+ 809 (NaClO₃)
4.	Tetragonal........	1.57 AgClO₃	+18.7	+ 761 (NaClO₃)

Both molecular heats are small and of opposite sign. The values for the isometric crystals are practically constant, showing that in this case there is little or no heat of dilution. In the other case, the variation, though small, is probably greater than the errors of experiment, so there appears to be a small heat of dilution.

The solubility of each salt in the other at different temperatures, given by Foote,[1] is as follows:

Temp.	Isometric. Molec. per cent. AgClO₃ in NaClO₃.	Tetragonal. Molec. per cent. NaClO₃ in AgClO₃.
12°..............................	14.33	50.04
25°.................	18.45	48.19
35°..............................	21.73	47.92
50°..............................	26.56	47.10

The amount of silver chlorate which can be taken up by the sodium salt to form mixed crystals increases with the temperature. As Table V shows, the process is accompanied by absorption of heat. The reverse is true in the case of the tetragonal crystals. In the relation of the heat of solution to the temperature coefficient of solubility, the law of Le Chatelier is, therefore, applicable to solid solutions as well as to solutions of other types. It may be well to add that, on the other hand, the van't Hoff equation

$$\frac{d \ln C}{dT} = \frac{Q}{2T^2},$$

[1] *Loc. cit.*

which gives for dilute liquid solutions a quantitative connection between the temperature coefficient of solubility and the heat of solution, does not apply.

SHEFFIELD CHEMICAL LABORATORY,
YALE UNIVERSITY, NEW HAVEN, CONN.

THE DISSOCIATION OF HYDROGEN INTO ATOMS.
Part I.   Experimental.

BY IRVING LANGMUIR AND G. M. J. MACKAY.

Some early measurements[1] of the heat loss by convection from heated tungsten wires in hydrogen showed that the loss increased at an abnormally high rate when extremely high temperatures were reached.

A little later[2] a series of measurements on the heat convection from various kinds of wires in different gases led to a general theory of convection from hot bodies, which makes possible the approximate calculation of heat losses from a wire at any temperature in any gas which behaves normally.

With hydrogen, the theory led to results in close agreement with the experiments, up to temperatures of about 2300° K. Above this, however, the observed heat loss increased rapidly until at 3300° K., it was over four times the calculated value.

This fact suggested that the hydrogen was partly dissociated into atoms at these high temperatures.

In a subsequent paper,[3] the theory of heat conduction in a dissociating gas was developed to apply to this case.[4] It was shown that the power required to heat the wire could be expressed as the sum of two terms, thus:

$$W = W_C + W_D \qquad , \qquad (1)$$

[1] Langmuir, Trans. Am. Electrochem. Soc., 20, 225 (1911).

[2] Langmuir, Phys. Rev., 34, 401 (1912).

[3] Langmuir, THIS JOURNAL, 34, 860 (1912).

[4] At the time of publication of the above mentioned paper, I was unaware that Nernst had previously (Boltzman, Festschrift, 1904, p. 904) developed a quantitative theory of the heat conduction in a dissociating gas, and had shown that the heat conductivity of nitrogen peroxide, determined by Magnanini, agreed well with that calculated by his equations from the known degree of dissociation of this substance. Nernst showed that the effect of the dissociation is to increase the heat conductivity of a gas by an amount equal to

$$Dq\frac{dc}{dT}.$$

He does not, however, show that this leads to the very simple and useful form of equation developed by the writer, namely,

$$W_D = SDq(C—C').$$

Nernst points out that the heat conductivity of gases may be used not only to detect dissociation qualitatively, as R. Goldschmidt (Thesis, Brussels, 1901) had shown, but in some cases to determine the degree of dissociation quantitatively. (I. LANGMUIR.)

Here W is the total power (in watts per centimeter) required to maintain the wire at a given temperature T_2.

W_C represents the part which is carried by ordinary heat conduction and follows the usual laws of heat convection, namely:[1]

$$W_C = S \int_{T_1}^{T_2} k dT = S(\varphi_2 - \varphi_1) \qquad (2)$$

S is called the shape factor and depends on the diameter of the wire and the nature of the gas, but is independent of the temperature of the wire. k is the coefficient of heat conductivity of the gas, W_D represents that part of the heat loss which is dependent on the dissociation of the gas. It was shown that W_D could be expressed thus:

$$W_D = SDq_1C_1 \qquad (3)$$

where S is the shape factor, D is the diffusion coefficient of hydrogen atoms through molecular hydrogen, q_1 is the heat of formation of hydrogen molecules from 1 g. of hydrogen atoms, and C_1 is the concentration of hydrogen atoms (grams per cc.) in the gas immediately in contact with the hot wire.

The experiments gave W directly (after subtracting the heat radiated from the hot wire). The value of W_C could be calculated by (2) and thus equation (1) led to a determination of W_D. By substituting in (3) the values of S and W_D, the product Dq_1C_1 was obtained from the results of the experiments.

It was then necessary to estimate the approximate value of D. This was done by guessing the probable free path of hydrogen atoms through hydrogen molecules by analogy with other gases and by then substituting this value in an equation, derived from the kinetic theory, which expresses the diffusion coefficient in terms of the normal free path.

Having thus chosen D and dividing this into the known value of Dq_1c_1, the product q_1c_1 was found. Van't Hoff's equation gives a relation between q_1 and the temperature coefficient of c_1. Since q_1 is nearly independent of the temperature, the temperature coefficient of c_1 must be practically equal to that of q_1c_1, so that in this way q_1 could be found. From this, the value c_1 and the degree of dissociation was then calculated.

The degree of dissociation of hydrogen into atoms (at atmospheric pressure) was thus calculated to be 1.2% at 2300° K., and 44% at 3100° K., and 84% at 3500° K. The heat of formation of the molecules from the atoms was given at 130,000 calories (for 2 g. of hydrogen).

These results seemed to conflict seriously with the measurements of the specific heat of hydrogen obtained by the explosion method. Pier[2] had

[1] *Phys. Rev., l. c.*
[2] *Z. Elektrochem.*, **15**, 536 (1909).

not recondense on replacing liquid air. The hydrogen may deposit on cooled glass surfaces, even in tubing at a considerable distance from the bulb. This hydrogen has remarkable chemical activity and will react with oxygen and phosphorus at room temperature. These effects are not due to the catalytic effect of finely divided metal deposits. The active hydrogen is not affected by an electrostatic field and therefore does not consist of hydrogen ions.

2. The active hydrogen thus produced can diffuse through long tubes (at low pressures) and can then dissolve in platinum (at 50°) and cause a marked increase in its electrical resistance and corresponding decrease in its temperature coefficient. Ordinary hydrogen, under similar conditions, will not do this. These effects have been described in some detail by Freeman.[1]

3. It has been found that tungstic oxide, WO_3, platinum oxide, PtO_2,[2] and many other substances, placed in a bulb containing a tungsten filament and hydrogen at very low pressures, rapidly become chemically reduced when the filament is heated to a temperature exceeding about 1700° K. although otherwise they are not acted on by hydrogen.

Many of these phenomena have been studied quantitatively in some detail, and the results seem consistently to be in accord with the theory that a portion of the hydrogen which comes into contact with the hot wire is dissociated into atoms. These, perhaps because of strong unsaturated chemical affinity, tend to adhere to glass surfaces even at room temperature. Some, however, leave the glass and wander further. Gradually the glass surfaces become charged with hydrogen atoms to such an extent that any fresh atoms striking the surface, combine, even at liquid air temperatures, with those already present. In case the atoms strike a metal surface such as platinum, they dissolve in it up to a considerable concentration.

The foregoing results afford satisfactory proof that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures.

There is, however, good reason to suspect that the actual values for the degree of dissociation previously given are considerably too high. The cause of this was thought to be an incorrect assumption as to the diffusion coefficient of hydrogen atoms through molecular hydrogen.

The remainder of the present paper deals with the results obtained by two methods which lead to more or less quantitative data on the dissociation, without necessitating any assumptions as to the magnitude of the diffusion coefficient.

[1] This Journal, 35, 927 (1913).

[2] Formed and deposited on the bulb by heating Pt at very high temperature in O_2 at low pressure or by passing a glow discharge between Pt electrodes in O_2 at low pressure.

The first method is based on measurements of the total heat losses from tungsten wires at a series of different pressures, ranging from 10 mm. up to atmospheric pressure.   If the previous results were correct, that is, that hydrogen is 44% dissociated at atmospheric pressure and 3100° K , then, at a pressure of 10 mm., the dissociation should be 96.5%   A further rise in temperature could then only slightly increase the degree of dissociation, for it is already close to the limit of 100%.   We see, then, from equation (3), that the heat loss under these conditions would have only a very small temperature coefficient   It was hoped, at the outset of these experiments, that the actual degree of dissociation could be determined from the decrease in the temperature coefficient of W_D as the pressure was progressively lowered.

The experiments to be described have shown, however, that even at 10 mm pressure the temperature coefficient of W_D is practically as great as at atmospheric pressure, showing that even at these low pressures the hydrogen around the wire is not nearly completely dissociated.   These experiments, however, give an upper limit to the degree of dissociation.

In the second method, measurements were made at very much lower pressures, from 0 01 mm. up to 0 2.   At the lowest pressures, the conditions should become very simple, for the molecules travel in straight lines directly from filament to bulb.   Under such conditions, the hydrogen atoms produced practically never return to the filament without having struck the bulb many times and having had ample opportunity of recombining. The filament is, therefore, struck only by hydrogen molecules, and from the formula

$$m = \sqrt{\frac{M}{2\pi RT}} p^1 \tag{5}$$

the rate at which the hydrogen molecules reach the surface may be calculated.   If, then, the heat loss be determined by experiment, the energy carried away by each molecule can be calculated.   If, by heating the filament to very high temperatures, a condition could be reached in which every hydrogen molecule which strikes the filament becomes dissociated, then those experiments would lead to a direct determination of the heat of formation (heat absorbed by dissociation) of hydrogen molecules In the absence of definite evidence that the dissociation is complete, the method gives at least a lower limit for the heat of formation.

Experiments on the Heat Losses from Tungsten Wires in Hydrogen.

1. *Higher Pressures.*—In the experiments upon which the former calculations of the dissociation were based, the measurements of heat loss

[1] Here m is the rate (in grams per sq cm per second), at which the hydrogen comes into contact with the filament   M is the molecular weight of H_2 (i e , 2), T is the temperature of the bulb, and p is the pressure of the hydrogen in the bulb   The derivation of this equation has been given in a previous paper (*Phys Rev* , *N S* , 2, 329 (1913)) and *Physik. Z.*, 14, 1273 (1913)

were made from short pieces of tungsten wire mounted vertically in a large glass tube open at the lower end, through which a fairly rapid stream of hydrogen passed. The temperature in most cases was determined from the resistance. The relation between resistance and temperature was, however, found by measurement of the intrinsic brilliancy of pieces of the same wire mounted in exhausted bulbs.

In the present experiments, it was desired to employ a series of different pressures of hydrogen around the filament, and furthermore, to avoid injury to the wire by impurities in the hydrogen.

The method adopted was therefore to mount single loop filaments of pure tungsten wire in large heater lamp bulbs (cylindrical bulbs about 25 cm. long and 7 cm. diameter) which were filled with pure, dry hydrogen at various pressures. These were then set up on the photometer bench and a series of simultaneous measurements of candle power, current and voltage were made. The color of the light emitted was also accurately matched against that from a standard lamp viewed through a special blue glass.[1]

Before filling the bulbs with hydrogen, they were exhausted to 0.1 micron pressure for an hour while heated to 360°, and the filaments were heated to a high temperature to drive off gases. The hydrogen was prepared electrolytically and was freed from oxygen and water vapor with extreme care.

Thirty lamps were made up for these experiments. Fifteen of these were filled with hydrogen at the following pressures· 1, 10, 25, 50, 100, 200 and 750 mm. Six were exhausted to a good vacuum in order to determine the amount of energy radiated. The remainder were filled with pure nitrogen at various pressures, to compare the heat loss in this gas with that in hydrogen.

The wire used in all lamps was 0.00706 cm. diameter. In every case it was welded to nickel leads with tungsten or molybdenum tips. The length of wire used in the hydrogen lamps ranged from 5 to 9 cm. and in the vacuum and nitrogen lamps, from 6 to 12 cm. It was necessary to use rather short lengths in hydrogen in order to be able to heat the wire to the melting point without using voltages over 200 volts.

Temperature Measurements.—The temperatures were determined, as has been usual in this laboratory, by the relation

$$T = \frac{11230}{7.029 - \log H} \tag{6}$$

where H is the intrinsic brilliancy of the filament in international candle power per sq. cm. of projected area. On this scale the melting point of

[1] This method has proved extremely accurate and serviceable as a means of comparing the temperatures of tungsten filaments. It is described in some detail by Langmuir and Orange. *Proc Amer Inst Elect Eng*, **32**, 1895 (1913).

tungsten proves to be 3540° K. (by direct experiment). This value we consider to be more probable than the lower values usually given.

The temperatures were also determined by two auxiliary methods: by measurement of the resistance and by matching the color of the emitted light against that of a standard provided with a blue screen.   In both these methods, however, the primary standard of temperature was the one given above, based on the intrinsic brilliancy of the filament.

It was found in nearly all experiments that the three methods gave concordant results.   The presence of hydrogen or nitrogen did not change either the resistance or the color of the light emitted from a filament set up at a given intrinsic brilliancy.   Discordant results were obtained only in the experiments in vacuum or low pressures of gas after the filament had been heated some time above 3200° K. and had evaporated so that the bulb had blackened and the diameter of wire had changed.

In order to avoid errors in temperature due to the cooling effect of the leads, the candle power was usually determined through a slit, one or two centimeters wide, placed horizontally in front of the lamp.   In this way, the intrinsic brilliancy can be determined with accuracy.

At temperatures below 1800° K., the candle power determinations were too inaccurate to be suitable for temperature measurements.   The temperatures were, therefore, found in these cases from the resistance, proper correction being made for the cooling effects of the leads.

Before making measurements on the lamps, they were thoroughly aged by running them for 24 hours with the filaments at a temperature of about 2400° K.   With the hydrogen and nitrogen of the purity used in these experiments, this treatment produced no perceptible injury of the filament. During the first few hours of aging, the filament, even in vacuum lamps, undergoes slight changes in resistance; and it was with this object, as well as to test the purity of the gases, that the lamps were subjected to the aging process.

The lamps were then set up on the photometer one by one, and measurements of current, voltage, candle power and color were made.   About 30 to 50 sets of readings were taken with each lamp, raising the voltage usually in steps of 2.5 to 5 volts at a time.   The temperature was thus gradually raised from 800° K., up to about 2900°.   Then a series of points was taken at descending temperatures and finally the temperatures were raised to temperatures of 3000° and more, frequently repeating some of the measurements at lower temperatures to see if the filament had undergone any change.   The readings up to 3000° K. could be taken without haste, as the filament undergoes only relatively slow changes below this temperature.   Above this temperature the readings were taken as rapidly as possible, and at wider intervals (usually 10 volts).   These precautions were especially necessary with the lamps containing less than 100 mm. of

gas. In those containing nearly atmospheric pressure of either hydrogen or nitrogen, there was never any perceptible darkening of the bulb, and the loss of material from the filament was extremely small, even when the temperature was raised several times very close to the melting point of the filament.

From the data thus obtained, the power consumption (in watts per centimeter of length), the temperature, and the resistance (per centimeter) were determined. The watts per cm. were plotted on semi-logarithmic paper against temperature and smooth curves drawn through the points.

Most of the points fitted very closely (within 1 or 2%) with the smoothed curves, and it was only rarely, at very low and at very high temperatures, that deviations as great as 5% were observed.

The results of these experiments are summarized in Table I. The energy *radiated* from the filament per second (in watts per centimeter of length) is given in the second column under the heading W_R. This was obtained from the lamps with well exhausted bulbs. The resistance (in ohms per centimeter) of the filament is given in the third column headed R. These values represent the averages of all the lamps. There was no appreciable difference in R for the gas filled and the vacuum lamps. The next six columns contain the data obtained from the bulbs containing hydrogen. The figures give directly the energy carried from the filament by the gas, the values tabulated being obtained by subtracting W_R from the observed total power consumption (in watts per cm.).

The last five columns contain similar data obtained from the nitrogen filled lamps.

Simple observation of these figures show the very striking difference in the effects in the two gases. In nitrogen, the values decrease steadily as the pressure is reduced, and in hydrogen, at the lower temperatures, the same decrease is observed. But at higher temperatures, in hydrogen, the power consumption is considerably greater at lower pressures than at atmospheric pressure.

The conclusions drawn from these measurements will be considered later, together with the results obtained at still lower pressures.

Lower Pressures.—In these experiments, measurements of the power consumption were made at a series of temperatures, with pressures ranging from 0.01 mm. up to 13 mm. The measurements were made while the lamps containing the filaments were connected to a vacuum system consisting of two McLeod gages (one for lower and one for higher pressures) and a Gaede mercury pump. The lamps were first exhausted at 360° for an hour and a trap immersed in liquid air placed directly below the lamps condensed the moisture given off from the glass.

The candle power was measured during the experiments by a portable Weber photometer. The characteristics in vacuum at temperatures

TABLE I

Temp °K	W/R	R	Watts per cm carried by hydrogen						Watts per cm carried by nitrogen					
			500 mm	200 mm	100 mm	50 mm	25 mm	10 mm	750 mm	200 mm	100 mm	50 mm	10 mm	1 mm
800	0 00	0 49	1 70	1 20	1 03	0 68								
900	0 01	0 57	2 15	1 50	1 29	0 80								
1000	0 02	0 65	2 60	1 80	1 52	0 95								
1100	0 03	0 72	3 02	2 10	1 80	1 09								
1200	0 05	0 80	3 50	2 46	2 05	1 25								
1300	0 08	0 87	4 08	2 86	2 17	1 44								
1400	0 11	0 95	4 72	3 33	2 70	1 65								
1500	0 15	1 03	5 50	3 90	3 13	1 92								
1600	0 21	1 11	6 32	4 45	3 64	2 20					0 40			
1700	0 29	1 20	7 15	5 10	4 22	2 50					0 48			
1800	0 38	1 29	8 04	5 75	4 88	2 92					0 58			
1900	0 50	1 39	9 02	6 49	5 64	3 6					0 67		0 30	0 09
2000	0 65	1 49	10 17	7 38	6 63	4 4			1 65	1 46	0 78	1 00	0 34	0 10
2100	0 83	1 59	11 56	8 44	7 85	5 4			1 86	1 60	0 90	1 08	0 38	0 11
2200	1 06	1 69	13 2	9 74	9 42	6 9		2 6	2 06	1 76	1 01	1 16	0 44	0 12
2300	1 31	1 79	15 2	11 2	11 4	8 9		3 4	2 26	1 91	1 12	1 25	0 50	0 13
2400	1 60	1 89	17 5	13 4	14 3	11 4		4 6	2 46	2 06	1 22	1 34	0 56	0 13
2500	1 92	1 99	20 7	16 4	17 8	14 5		6 0	2 68	2 22	1 34	1 42	0 60	0 14
2600	2 33	2 09	24 2	19 9	21 5	18 5		8 0	2 90	2 36	1 45	1 51	0 64	0 14
2700	2 70	2 20	28 8	25 5	27 6	23 5		10 2	3 12	2 52	1 58	1 60	0 68	0 15
2800	3 30	2 30	34 8	32 5	35 3	29 8		13 4	3 34	2 68	1 73	1 69	0 72	0 15
2900	3 86	2 41	41 1	42 0	45 1	36 7		17 0	3 56	2 84	1 87	1 78	0 75	0 16
3000	4 46	2 52	49 2	54 0	56 7	45 1		22 3	3 84	3 00	2 00	1 87	0 78	0 16
3100	5 13	2 62	58 0	67 0	70 4	57 1		27 2	4 06	3 16	2 14	1 97	0 81	0 16
3200	5 98	2 72	70 0	84 0	88 2	68 6		33 4	4 30	3 32	2 27	2 06	0 84	0 17
3300	6 94	2 82	82 0	101 0	101 0	84 0		41 6	4 54	3 49	2 43	2 16	0 89	0 17
3400	8 08	2 93	94 0	115 0	110 0	101 0		49 8	4 76	3 66	2 58	2 26	0 96	0 18
3500	9 41	3 05	108 0	136 0	118 0	118 0		60 0	5 00	3 83	2 72	2 36	1 01	0 18

ranging from 1500 to 2500° K. were first determined and then a few centimeters (pressure) of pure hydrogen was admitted to the system and pumped out to a pressure of 13 mm.   A series of measurements of current, voltage and candle power was again made.   In this way, in the first experiment, the characteristics were measured at pressures of 13.1, 6.5, 2 5, 1.2, 0.53, 0.218, 0.102 and 0 045, 0.020 and 0.010 mm and at 0.0001 mm. In a second experiment, measurements at a few pressures were made as a check on the preceding.

In the third experiment, made a few weeks later, a much more complete series of measurements was made, extending the range of observations from 1100° to 2900° K.   Higher temperatures were avoided, in order not to cause any evaporation of the filament   The pressures employed in this set of tests were 4.4, 1 10, 0.207, 0 039, 0.015 and 0 00007 mm. At each pressure about 30 readings at different temperatures were taken.

The results of the third experiment were in excellent agreement with those of the first two.   Since the former covered so much wider a range, only these results are given in this paper.

The tungsten wire used for these experiments was taken from the same spool as that used in the experiments at higher pressures

The filament was mounted horizontally in a straight piece 9.85 cm. long Because of the cooling effect of the leads, it was assumed that the effective length of the wire for calculation of the watts per centimeter was 9.4 cm. The bulb was a cylindrical bulb with rounded ends, about 10 cm diameter and 18 cm. long, and the filament was supported in its axis

TABLE II.

Temp ° K	W_R	R	Heat carried by hydrogen watts per cm				
			4 40 mm	1 10 mm	0 207 mm	0 039 mm	0 015 mm
1100	0 022	0 60	0 26	0 09	0 020	0 004	0 002
1200	0 037	0 70	0 31	0 11	0 024	0 005	0 002
1300	0 060	0 80	0 36	0 13	0 030	0 006	0 002
1400	0 095	0 89	0 41	0 16	0 038	0 007	0 003
1500	0 138	0 98	0 47	0 19	0 050	0 009	0 004
1600	0 192	1 07	0 55	0 22	0 066	0 012	0 006
1700	0 268	1 15	0 65	0 28	0 088	0 019	0 008
1800	0 36	1 24	0 82	0 36	0 125	0 032	0 012
1900	0 48	1· 33	1 09	0 52	0 21	0 06	0 019
2000	0 62	1 42	1 44	0 85	0 34	0 10	0 031
2100	0 78	1 52	2 06	1 27	0 53	0 16	0 055
2200	0 98	1 62	2 98	1 81	0 73	0 22	0 092
2300	1 23	1 72	4 37	2 62	0 99	0 29	0 120
2400	1 55	1 82	5 98	3 56	1 27	0 37	0 148
2500	1 82	1 92	8 21	4 85	1 58	0 42	0 178
2600	2 20	2 02	11 0	5 49	1 82	0 48	0 189
2700	2 67	2 12		6 23	1 96	0 50	0 191
2800	3 20	2 23		6 97	1 98	0 50	0 191
2900	3 80	2 34		7 61	1.99	0 50	0 191

The data obtained by these experiments are given in Table II. In the second and third columns are given the characteristics of the filament in good vacuum (0.00007 mm.). W_R is expressed in watts per centimeter, and R in ohms per centimeter. The figures in the other columns give the differences between the observed power consumption at different pressures and those in vacuum.

Discussion of Experimental Results.

The experimental data contained in Tables I and II give, as a function of both temperature and pressure, the total heat carried by the surrounding hydrogen from a heated tungsten filament in this gas.

It has been shown in the previous papers that this energy carried by the gas can be resolved into two parts, W_C and W_D.

$$W = W_C + W_D \qquad (1)$$

The temperature coefficient of W_C is given by

$$W_C = S(\varphi_2 - \varphi_1) \qquad (2)$$

where

$$\varphi = \int_0^T k\,dT.$$

In the previous paper, S was calculated from results obtained with gases other than hydrogen. This method of calculation of S, although giving an approximation good enough for most purposes, may be open to criticism. In the present case, therefore, it has been thought better to determine S directly from the experimental results of Tables I and II.

The values of $\varphi_2 - \varphi_1$ were taken from the data given in the previous paper,[1] in which φ was calculated from the heat conductivity of hydrogen as determined by Eucken[2] and from the measurements of the viscosity of hydrogen by Fisher[3].

By trial a value of S was found, which, when multiplied by $\varphi_2 - \varphi_1$, would give the best agreement with the values of W observed at temperatures so low that W_D was negligible. At higher temperatures, W_D was obtained by subtracting $S(\varphi_2 - \varphi_1)$ from W. The logarithm of W_D was plotted against $1/T$ from the data at rather low temperatures (1700–2500° K.). It is only in this range of temperatures that the calculated values of W_D are materially affected by errors in the value S. By trial a value of S was finally chosen which would give most nearly a straight line relation between log W_D and $1/T$.

These values of S have been used to calculate W_D and the results are given in Table III.

[1] *Physic. Rev. l. c.*
[2] *Physik. Z , 12, 1101 (1911).*
[3] *Physic. Rev., 24, 385 (1907).*

TABLE III

W_D from Experiments with Hydrogen.

Temp. °K	$\epsilon_r - \epsilon_i$ watts per cm	750 mm s 1.25	200 mm s 0.88	100 mm s 0.72	50 mm s 0.56	25 mm s 0.40	10 mm s 0.21	4.40 mm s 0.096	1.10 mm s 0.040	0.287 mm s 0.009	0.039 mm s 0.002	0.015 mm s 0.0008
800	1 28	+0 10	+0 13	+0 10		+0 17		+0 02	—0 01	—0 002		::
900	1 68	+0 05	+0 02	+0 07		+0 13		+0 02	—0 01	—0 003	:	::
1000	2 05	+0 04	0 00	+0 04		+0 13		+0 03	—0 01	—0 001	—0 001	0 000
1100	2 50	—0 10	—0 10	—0 01		+0 09		+0 03	0 00	+0 002	—0 001	0 000
1200	3 00	—0 25	—0 18	—0 12		+0 05		+0 04	—0 01	+0 009	+0 000	+0 001
1300	3 45	—0 24	—0 18	—0 32		+0 06		+0 07	+0 02	+0 020	+0 002	0 000
1400	3 95	—0 22	—0 15	—0 16		+0 07		+0 11	+0 05	+0 037	0 008	0 000
1500	4 50	—0 13	—0 06	—0 13		+0 12		+0 22	0 11	0 068	0 019	+0 002
1600	5 05	—0 01	0 00	—0 02		+0 17		0 43	0 24	0 15	0 05	+0 003
1700	5 65	+0 09	+0 13	+0 12		+0 24		0 71	0 54	0 27	0 09	+0 007
1800	6 28	+0 19	+0 23	+0 33		+0 41		1 26	0 94	0 45	0 14	0 013
1900	6 93	+0 35	+0 39	0 61		0 8	1 0	2 10	1 45	0 65	0 20	0 025
2000	7 62	+0 64	+0 67	1 10	2 4	1 3	1 7	3 42	2 22	0 90	0 27	0 048
2100	8 34	1 15	1 10	1 8	4 0	2 1	2 7	4 95	3 13	1 17	0 35	0 085
2200	9 13	1 80	1 70	2 8	6 1	3 2	3 9	7 10	4 19	1 48	0 40	0 112
2300	9 90	2 8	2 5	4 2	8 9	4 9	5 8	9 8	5 00	1 71	0 45	0 139
2400	10 70	4 2	4 0	6 5	12 5	7 1	7 8		5 7	1 84	0 47	0 169
2500	11 53	6 3	6 3	9 4	16 7	9 9	10 8		6 4	1 85	0 47	0 179
2600	12 36	8 8	9 0	12 5	22 4	13 5	14 2		7 0	1 85	0 47	0 180
2700	13 28	12 2	13 8	18 0	30 0	18 2	19 3					0 180
2800	14 22	17 0	20 0	25 0	38 0	24 0	24 0					0 180
2900	15 22	22 0	29 0	34 0	48 0	30 0	30 0					
3000	16 20	29 0	40 0	45 0	59 0	38 6	38 0					
3100	17 13	37 0	52 0	58 0	74 0	48 1	46 0					
3200	18 17	47 0	68 0	75 0	90 0	58 0	56 0					
3300	19 21	58 0	84 0	96 0	107 0	71 0						
3400	20 35	69 0	97 0	117 0								
3500	21 50	81 0	117 0									

TABLE IV.

"W_D" from Experiments with Nitrogen

T_1 °K	$\varphi_2-\varphi_1$ watts per cm	750 mm S= 1 41	200 mm S= 1 15	100 mm S= 1 06	50 mm S= 0 75	10 mm. S= 0 43	1 mm. S= 0 10
1100	0 43			—0 06			
1200	0 49			—0 04			.
1300	0 56			—0 01			+0 03
1400	0 63			—0 04		+0 03	+0 04
1500	0 73			+0 01		+0 03	+0 04
1600	0 82			+0 03		+0 03	+0 04
1700	0 92			+0 03		+0 04	+0 04
1800	1 03			+0 03		+0 06	+0 03
1900	1 13			+0 02		+0 07	+0 03
2000	1 25	—0 11	+0 02	+0 01	+0 07	+0 06	+0 02
2100	1 36	—0 04	+0 04	+0 01	+0 06	+0 06	+0 01
2200	1 49	—0 01	+0 05	0 00	+0 04	+0 04	0 00
2300	1 61	—0 01	+0 06	+0 02	+0 05	+0 03	0 00
2400	1 74	+0 01	+0 06	+0 02	+0 04	+0 00	—0 01
2500	1 87	+0 04	+0 07	+0 02	+0 02	+0 02	—0 03
2600	2 02	+0 05	+0 04	—0 00	0 00	—0 06	—0 03
2700	2 16	+0 07	+0 04	—0 02	—0 02	—0 09	—0 05
2800	2 31	+0 08	+0 02	—0 03	—0 04	—0 10	—0 06
2900	2 47	+0 08	0 00	—0 04	—0 07	—0 10	—0 07
3000	2 63	+0 13	—0 02	—0 07	—0 10	—0 11	—0 08
3100	2 79	+0 12	—0 04		—0 12		
3200	2 96	+0 13	—0 08		—0 16		
3300	3 13	+0 13	—0 11		—0 29		
3400	3 31	+0 09	—0 14	'	—0 22		
3500	3 49	+0 08	—0 18		—0 26		

The results in Table III were obtained from the data in Tables I and II, merely by subtracting the product of S (given at the head of each column of Table III) by $\varphi_2-\varphi_1$ (given in second column of Table III).

The data on the heat losses from tungsten wires in nitrogen given in Table I, was used in a similar way to calculate $W—W_C$ and the results are given in Table IV. The values of $\varphi_2-\varphi_1$ in this table are calculated from the viscosity and heat conductivity of nitrogen.[1]

A comparison of Tables III and IV shows clearly the very great difference between hydrogen and nitrogen. With nitrogen the heat loss increases with the temperature very nearly proportionally to $\varphi_2-\varphi_1$. The differences observed and tabulated are not greater than the possible experimental errors. In the case of hydrogen, up to temperatures of 1500–1700° K., the results are similar to those of nitrogen, that is, there is no evidence that the differences between W and W_C are anything more than experimental errors. But at very high temperatures W_D increases

[1] See *Physic. Rev., l. c.*

very rapidly, and becomes 50 or 100 times as large as the possible experimental error.

In the second part of this paper, these data will be used to calculate the degree of dissociation and the heat of formation of hydrogen molecules. The experiments at low pressures lead to a somewhat detailed knowledge of the mechanism of the reaction taking place on the surface of the wire.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

THE ADDITION COMPOUNDS OF ORGANIC ACIDS IN PAIRS.

BY JAMES KENDALL.
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In a recent communication[1] the author has shown, by the application of the freezing-point method, that a large number of organic acids form addition compounds with dimethylpyrone, and that these compounds are to be regarded as true oxonium salts. The reaction is best expressed by the equation:
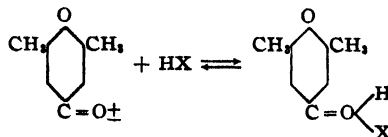
The formation of an equimolecular addition compound is thus considered to be due to the basic (or unsaturated) properties of the group $>C = O\underline{+}$, in which oxygen functions as a quadrivalent atom.

This same group, $>C = O\underline{+}$, is present in all organic acids themselves. Consequently it appeared probable that, if the acidic properties of an organic acid could be sufficiently suppressed, the basic nature of the group $>C = O\underline{+}$ would become evident and formation of addition compounds with other substances could be obtained. Now the acidic properties of a weak acid can obviously be reduced to a minimum by the presence of a second, much stronger acid. In the present investigation, therefore, the validity of the general conclusions drawn in the previous paper is tested by this method—the examination of systems containing two organic acids of widely divergent strengths.

The experimental details and the main principles of the method followed have already been described in full. The formation of an addition compound can be immediately deduced from the freezing-point curve of a two-component system by the appearance of a maximum on the curve; the position of the maximum indicates the composition of the compound.

[1] Kendall, THIS JOURNAL, 36, 1222 (1914).

Since these addition reactions are reversible, any compound formed is partially dissociated into its components on fusion; the extent of dissociation is indicated by the form of the curve near the maximum. In the previous investigation it was shown that the degree of dissociation (in other words, the relative stability of the salt) is a function of the strength of the acid used.

For the present work, the following acids were selected from among those previously employed:

SERIES A—WEAK ACIDS		SERIES B—STRONG ACIDS	
Acid	100 K	Acid	100 K
Benzoic .	0 0060	Trichloroacetic	121 0
o-Toluic	0 0120	Dichloroacetic	5 14
m-Toluic	0 00514	Chloroacetic	0 155
p-Toluic	0 00515		
α-Toluic	0 00556		
Cinnamic . .	0 00355		
Acetic	0 00180		
Crotonic	0 00204		

The terms "weak" and "strong" are here applied to the acids in a relative sense only. The dissociation constants are those given by Ostwald;[1] for the stronger acids the values must be regarded as merely approximate.[2]

It will be seen that the acids under A are all of approximately the same strength, while the acids under B form a series covering a very wide range. By such a choice of material it was made possible to subject the views of the author on oxonium salt formation, as expressed above, to a very rigorous test. The tendency to form addition products should increase with the difference in acidic strength of the two components of the system. Acids of widely divergent strengths should readily give addition compounds, acids of similar strengths should show little tendency towards compound formation. In the above series, consequently, we should expect addition compounds (if produced at all) to be most stable in systems containing trichloroacetic acid, less stable when dichloroacetic acid is present, still less stable when chloroacetic acid is employed.

. This was, indeed, found to be the case throughout. With trichloroacetic acid, equimolecular addition compounds were isolated in five out of eight cases. In the remaining three systems, the form of the freezing-point curve showed that such compounds were undoubtedly present in solution, but, owing either to persistent supercooling or to extremely low fusion points, could not be isolated. The form of the curves indicated also that the compounds were fairly considerably dissociated into their components on fusion, and were uniformly much less stable than those

[1] Ostwald, *Z. physik. Chem.*, **3**, 418 (1889).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912); *Meddel från K. Vet.-Akads Nobel-institut*, Band **2**, No 38 (1913).

obtained in the previous investigation with dimethylpyrone. This was to be expected, since there the components were one acidic and one basic, while here both are primarily acidic.

With systems containing dichloroacetic acid, addition products were obtained in two out of eight cases. In the remaining six, compounds were present in solution, but could not be isolated. (All solutions containing dichloroacetic acid were extremely difficult to investigate, owing to persistent supercooling.) The compounds obtained were much less stable than those with trichloroacetic acid.

From systems containing chloroacetic acid no addition compounds were obtained, and the curves indicate that the tendency towards com-

Fig. 1

I   o-Toluic acid—Trichloroacetic acid. Subtract 130°
      from temperature scale.
II m-Toluic acid—Trichloroacetic acid. Subtract 100°
      from temperature scale.
III α-Toluic acid—Trichloroacetic acid. Subtract 70°
      from temperature scale.
IV α-Toluic acid—Dichloroacetic acid. Subtract 20°
      from temperature scale.
V   α-Toluic acid—Chloroacetic acid. Add 60° to
      temperature scale

Fig. 2

I.   Benzoic acid—Trichloroacetic acid. Temperature
       scale correct.
II. Benzoic acid—Dichloroacetic acid. Subtract 90°
       from temperature scale.
III. Benzoic acid—Chloroacetic acid. Subtract 20°
       from temperature scale.
IV. Benzoic acid—Acetic acid. Add 50° to tempera-
       ture scale.
V.   Cinnamic acid—Dichloroacetic acid. Subtract 110°
       from temperature scale.

pound formation is extremely slight. This is in keeping with the relatively weak acidic nature of chloroacetic acid. The examination of several similar systems (in which both acids taken were either from Series A or Series B) confirmed the conclusion that, with acids of only slightly divergent strengths, no addition compounds are formed.

The experimental results are given in the tables below; these are arranged as in the previous paper. A few typical curves are shown in the accompanying diagrams.

Experimental.

1. **Benzoic Acid—Trichloroacetic Acid.**—The equimolecular compound, $C_6H_5.COOH$, $CCl_3.COOH$, was obtained, m. p. 36.4° (by extrapolation). The compound is not stable at its maximum, and crystallizes only from solutions containing excess of trichloroacetic acid. The freezing-point curve is shown in Fig. 2.

(a) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100.0	80.1	68.3	63.6	60.1	55.5	52.0	47.1
T	121.0	105.6	89.7	79.9	72.8	64.0	54.4	43.1

(b) Solid phase, $C_6H_5.COOH$, $CCl_3.COOH$.

% $C_6H_5.COOH$	42.9	39.2	33.3	31.5
T	34.6	32.6	28.1	26 6

(c) Solid phase, $CCl_3.COOH$.

% $C_6H_5.COOH$	26.7	22.5	21.9	16.7	9.4	0
T	32.3	36.9	38.0	45.0	50.5	57.3

2. **o-Toluic Acid—Trichloroacetic Acid.**—The compound $C_7H_7.COOH$, $CCl_3.COOH$ was obtained, m. p. 52.9°; stable at its maximum. (See Fig. 1.)

(a) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	90.0	81.2	73.9	67.2	58.3	53.8
T	103 4	97.6	90.5	83.9	76.8	64.7	55.7

(b) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	49.8	45.5	40.8	37.6	33.1	28.8	23.5
T	54.9	52.6	51.8	50.4	48.1	45.1	39.4

(c) Solid phase, $CCl_3.COOH$.

% $C_7H_7.COOH$	27.9	21.5	15.0	8.7	0
T	30.7	38.9	45.5	51.3	57.3

3. **m-Toluic Acid—Trichloroacetic Acid.**—The compound $C_7H_7.COOH$, $CCl_3.COOH$ was obtained, unstable at its maximum; m. p. 37.4° (by extrapolation). (See Fig. 1.)

(a) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	89.3	78.1	65.7	60.2	55.7	51.4
T	107.6	100.2	89.8	75.3	66.6	56.9	45.4

(b) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	49.6	45.8	41.9	36.7
T	37.3	36.3	34.6	31.3

(c) Solid phase, $CCl_3.COOH$.

% C_7H_7 COOH	31 4	26 5	21 0	15 9	7 7	0
T	26 2	32 4	38 6	44 1	51 5	57 3

4. p-Toluic Acid—Trichloroacetic Acid.—An equimolecular compound was obtained, unstable at its maximum, m. p. 69.0° (by extrapolation).

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	87 2	76 2	65 5	57 6	50 1	44 8	40 0	36 9
T	178 6	170 4	160 1	145 9	131 9	115 5	100 2	84 1	69 1

(b) Solid phase, C_7H_7 COOH, CCl_3 COOH

% C_7H_7.COOH	34 5	30 5	25 7	22 3	18 1
T	63 5	60 3	55 7	51 8	45 0

(c) Solid phase, CCl_3 COOH

% C_7H_7 COOH	12 9	6 9	0
T	46 6	52 2	57 3

5. α-Toluic Acid—Trichloroacetic Acid.—No compound was here isolated. The curve is shown in Fig 1.

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	90 5	81 4	70 8	63 1	55 4	47 9
T	76 7	70 8	63 3	51 7	40 1	25 9	9 2

(b) Solid phase, CCl_3 COOH.

% C_7H- COOH	41 2	34 9	28 4	20 8	11 7	0
T	10 2	21 2	31 3	41 2	49 3	57 3

6. Cinnamic Acid—Trichloroacetic Acid.—The compound C_8H_7 COOH, CCl_3.COOH was obtained, unstable at its maximum, m p 63.0° (by extrapolation)

(a) Solid phase, C_8H_7 COOH

% C_8H_7 COOH	100 0	87 0	76 1	65 8	56 6	50 3
T	136 8	122 2	108 5	94 8	79 9	68 5

(b) Solid phase, C_8H_7 COOH, CCl_3 COOH

% C_8H_7 COOH	45 3	41 4	35 3	29 2	25 9
T	62 1	59 7	55 7	49 3	44 9

(c) Solid phase, CCl_3 COOH

% C_8H_7 COOH	24 8	19 7	17 4	9 3	0
T	36 1	42 5	45 0	51 1	57 3

7. Acetic Acid—Trichloroacetic Acid.—No compound was here isolated.

(a) Solid phase, CH_3 COOH

% CH_3 COOH	100 0	91 3	84 6	75 7	69 0
T	16 4	9 9	3 1	—10 1	—25 3

(b) Solid phase, CCl_3 COOH

% CCl_3 COOH	51 0	46 1	38 5	30 2	22 5	12 8	0
T	— 13 3	— 0 1	15 4	28 4	37 6	47 3	57 3

8. Crotonic Acid—Trichloroacetic Acid.—Here also no compound was isolated.

(a) Solid phase, C_3H_5 COOH

% C_3H_5 COOH	100 0	91 0	82 7	75 7	65 7	60 0	54 2	49 9
T		71 0	63 7	53 9	44 2	27 5	16 1	2 1	—9 9

(b) Solid phase, CCl_3 COOH

% C_3H_5 COOH	45 1	40 7	34 4	26 6	19 1	10 2	0
T	—	12 7	1 2	16 4	30 4	40 3	49 6	57 3

9. Benzoic Acid—Dichloroacetic Acid. – The compound C_6H_5.COOH, $CHCl_2$.COOH was obtained, unstable at its maximum, m p 58 2° (by extrapolation) The freezing-point curve is shown in Fig 2

(a) Solid phase, C_6H_5 COOH

% C_6H_5 COOH	100 0	81 5	70 7	61 1	50 8	48 4	45 7
T	121 0	104 0	91 6	79 1	64 6	61 2	56 7

(b) Solid phase, C_6H_5 COOH, $CHCl_2$ COOH

% C_6H_5 COOH	44 3	40 2	37 4	34 9	29 4	25 3	16 9	11 6	8 3	5 4
T	57 8	57 2	56 4	55 6	52 8	50 1	42 6	33 6	25 5	15 3

(c) Solid phase, $CHCl_2$ COOH

% C_6H_5 COOH	1 8	0
T	8 6	9 7

10. o-Toluic Acid—Dichloroacetic Acid.—No addition compound was here isolated

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	89 5	78 6	69 1	60 7	51 2	43 0	37 9	28 2	20 4	14 4
T	103 4	97 1	89 5	81 6	74 1	63 0	52 1	44 9	28 4	13 0	—1 9

(b) Solid phase, $CHCl_2$ COOH

% C_7H_7 COOH	12 5	7 1	0
T	—1 0	3 9	9 7

11. m-Toluic Acid—Dichloroacetic Acid.—Here also no addition compound was isolated

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	87 4	74 6	66 1	56 4	46 4	35 9	28 2	23 0
T	107 6	98 5	87 5	79 4	68 2	53 8	35 8	19 9	6 1

(b) Solid phase, $CHCl_2$ COOH

% C_7H_7 COOH	17 1	11 0	6 1	0
T	—6 1	—0 2	4 2	9 7

12. p-Toluic Acid—Dichloroacetic Acid.—No compound was isolated

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	85 1	71 6	59 5	50 0	40 9	33 1	26 1	20 4	15 5	10 8
T	178 6	168 1	154 9	139 6	125 2	109 0	91 3	75 2	59 7	42 3	23 1

(b) Solid phase, $CHCl_2$ COOH

% C_7H_7 COOH	5 2	0
T..	5 1	9 7

13. α-Toluic Acid—Dichloroacetic Acid.—No compound was isolated. (See Fig. 1.)

(a) Solid phase, C_7H_7 COOH

% C_7H_7.COOH	100 0	93 3	81 4	71 8	63 9	59 2	50 0	42 9	36 9
T	76 7	72 4	63 4	53 6	43 9	37 6	22 3	9 0	—5 5

(b) Solid phase, $CHCl_2$ COOH

% C_7H_7 COOH	25 9	15 3	7 5	0
T	—14 6	—3 3	3 5	9 7

14. Cinnamic Acid—Dichloroacetic Acid.—The equimolecular compound C_6H_7 COOH, $CHCl_2$ COOH was obtained, unstable at its maximum, m. p. 80 1°. (See Fig. 2.)

(a) Solid phase, C_6H_7 COOH

% C_6H_7 COOH	100 0	86 1	74 1	62 8	55 0	51 5
T	136 8	124 3	111 0	97 6	86 1	80 0

(b) Solid phase, C_6H_7 COOH, $CHCl_2$ COOH

% C_6H_7 COOH ..	51 5	50 0	44 8	37 3	29 8	24 6	17 1	12 8	7 8	6 0	4 1
T	80 0	80 1	79 7	77 8	74 2	69 6	61 4	54 0	42 8	35 7	24 7

(c) Solid phase, $CHCl_2$ COOH

% C_6H_7 COOH	1 6	0
T	8 6	9 7

15. Acetic Acid—Dichloroacetic Acid.—No addition compound was isolated. The central portion of the curve could not be completed, since at the very low temperature required for solidification the mixture sets to a hard, glassy mass.

(a) Solid phase, CH_3 COOH

% CH_3 COOH	100 0	91 4	79 2	70 5	63 6	55 0
T	16 4	10 3	— 0 7	—10 8	—21 5	—37 0

(b) Solid phase, $CHCl_2$ COOH

% CH_3 COOH	43 4	29 7	17 9	8 6	0
T	—40 8	—18 2	— 4 2	3 9	9 7

16. Crotonic Acid—Dichloroacetic Acid.—No addition compound could be isolated.

(a) Solid phase, C_3H_5 COOH

% C_3H_5 COOH	100 0	93 6	86 8	80 6	71 1	65 3	55 8	47 4	40 4
T	71 0	65 5	59 1	52 6	41 4	34 0	20 5	5 1	—9 7

(b) Solid phase, $CHCl_2$ COOH

% C_3H_5 COOH	31 0	17 1	8 9	0
T	—18 5	—4 2	2 7	9 7

17. Benzoic Acid—Chloroacetic Acid.—No compound was obtained in any system containing chloroacetic acid. The freezing-point curve is given in Fig. 2.

(a) Solid phase, C_6H_5 COOH.

% C_6H_5 COOH	100 0	81 0	69 8	58 5	52 9	44 2	38 6	32 0
T	121 0	107 2	96 8	86 1	80 4	69 9	62 4	52 6

(b) Solid phase, CH_2Cl COOH

% C_6H_5 COOH	25 1	21 1	14 4	5 9	0
T	48 7	50 7	54 5	58 6	61 4

18. o-Toluic Acid—Chloroacetic Acid.

(a) Solid phase C_7H_7 COOH

% C_7H_7 COOH	100 0	89 1	77 0	66 4	57 4	50 5	44 4	38 2	32 4
T	103 4	97 0	89 6	82 3	75 5	70 2	64 9	58 8	52 3

(b) Solid phase CH_2Cl COOH

% C_7H_7 COOH	27 5	22 1	16 5	11 5	5 8	0
T	47 9	50 7	53 3	55 7	58 5	61 4

19. m-Toluic Acid—Chloroacetic Acid.

(a) Solid phase C_7H_7 COOH

% C_7H_7 COOH	100 0	90 1	79 6	68 4	56 9	45 2	35 7
T	107 6	101 0	93 6	84 7	75 3	64 1	53 9

(b) Solid phase, CH_2Cl COOH

% C_7H_7 COOH	28 4	21 2	14 4	7 7	0
T	46 7	50 5	54 2	57 7	61 4

20. p-Toluic Acid—Chloroacetic Acid.

(a) Solid phase, C_7H_7 COOH

% C_7H_7 COOH	100 0	83 1	70 4	56 9	45 4	34 0	22 7	17 1	12 9
T	178 6	167 2	155 8	141 8	128 5	114 0	95 5	83 1	71 1

(b) Solid phase CH_2Cl COOH

% C_7H_7 COOH	9 3	4 7	0
T	56 8	59 1	61 4

21. α-Toluic Acid—Chloroacetic Acid. - The freezing-point curve is shown in Fig 1

(a) Solid phase C_7H_7 COOH

% C_7H_7 COOH	100	89 5	80 9	72 5	64 8	56 6	49 9
T	76 7	70 1	63 8	56 9	49 9	42 3	35 7

(b) Solid phase CH_2Cl COOH

% C_7H_7 COOH	41 6	32 9	23 9	14 9	6 7	0
T	33 6	40 0	46 7	52 7	57 9	61 4

22. Cinnamic Acid—Chloroacetic Acid.

(a) Solid phase, C_8H_7 COOH

% C_8H COOH	100	89 3	77 5	68 0	54 4	44 7	36 4	31 4
T	136 8	128 2	118 6	109 0	95 9	83 8	70 2	60 5

(b) Solid phase, CH_2Cl COOH

% C_8H_7 COOH	25 0	19 0	13 9	8 2	0
T	48 3	51 2	54 0	57 1	61 4

23. Acetic Acid—Chloroacetic Acid.

(a) Solid phase, CH₃ COOH

% CH₃ COOH	100	91 8	79 6	71 0			
T	16 4	10 7	1 7	—4 5			

(b) Solid phase, CH₂Cl COOH

% CH₃ COOH	71 0	62 0	50 3	40 3	29 4	15 5	0
T	5 0	12 8	22 2	29 7	38 0	49 4	61 4

24. Crotonic Acid—Chloroacetic Acid.

(a) Solid phase C₃H₅ COOH

% C₃H₅ COOH	100	91 2	83 4	75 4	65 9	56 5
T	71 0	64 4	57 7	50 7	41 1	30 9

(b) Solid phase CH₂Cl COOH

% C₃H₅ COOH	46 8	38 6	30 0	19 9	10 4	0
T	29 9	36 5	42 6	50 0	55 8	61 4

25. Benzoic Acid—α-Toluic Acid.

—In this and the two following systems the acids are both from Series A, no compound formation was indicated

(a) Solid phase, C₆H₅ COOH

% C₆H₅ COOH	100	91 0	82 1	70 0	57 9	48 7	38 3
T	121 0	115 2	108 5	97 8	85 3	74 0	57 4

(b) Solid phase, C₇H₇ COOH

% C₆H₅ COOH	28 9	18 9	10 1	0
T	56 9	63 7	69 5	76 7

26. Benzoic Acid—Cinnamic Acid.

(a) Solid phase, C₆H₅ COOH

% C₆H₅ COOH	100	86 8	76 9	69 9	61 7
T	121 0	111 0	102 0	95 4	87 2

(b) Solid phase, C₈H₇ COOH

% C₆H₅ COOH	52 5	42 3	33 1	19 9	9 6	0
T	87 3	100 5	109 5	121 5	130 1	136 8

27. Benzoic Acid—Acetic Acid.

—The freezing-point curve is shown in Fig 2

(a) Solid phase, C₆H₅ COOH

% C₆H₅ COOH	100	87 6	72 6	61 0	50 6	43 4	35 3	28 3	20 8	14 5
T	121 0	111 5	100 3	90 1	79 1	71 5	60 9	50 9	38 2	19 2

(b) Solid phase, CH₃ COOH

% C₆H₅ COOH	9 7	5 2	0
T	10 4	13 0	16 4

28. Chloroacetic Acid—Dichloroacetic Acid.

—In this and the following systems the acids are both from Series B, no addition compounds were isolated

(a) Solid phase, CH₂Cl COOH

% CH₂Cl COOH	100	90 1	82 5	75 8	66 4	54 0	40 4	32 7
T	61 4	56 8	52 5	47 5	40 5	29 6	10 8	—5 5

(b) Solid phase, CHCl₂ COOH.

% CH₂Cl COOH	24 7	12 2	0
T	—5 8	2 8	9 7

29. Chloroacetic Acid—Trichloroacetic Acid.

(a) Solid phase, CH₂Cl COOH

% CH₂Cl COOH	100	84 8	74 5	65 5	58 2	51 4
T		61 4	53 5	46 5	38 9	31 0	22 4

(b) Solid phase, CCl₃ COOH

% CH₂Cl COOH	41 7	31 9	24 1	15 5	0
T	24 3	33 2	39 9	46 1	57 3

30. Dichloroacetic Acid—Trichloroacetic Acid.

(a) Solid phase, CHCl₂ COOH

% CHCl₂ COOH	100	93 7	82 2	68 7
T	9 7	7 0	1 0	—7 9

(b) Solid phase, CCl₃ COOH

% CHCl₂ COOH	56 9	46 5	31 8	21 2	12 2	0
T	—0 6	14 5	32 9	42 5	49 6	57 3

Consideration of Results.

The general conclusions of the investigation have already been stated in the introduction. In the following pages, by closer examination of the freezing-point curves obtained, some quantitative results are deduced and discussed

From the diagrams given, it will be seen that the freezing-point curves are different in type, even where no addition compound is isolated, according to which acid of Series B is present in the system. In systems containing chloroacetic acid, the curves obtained are approximately linear, the change in slope as the eutectic point is approached being very slight In systems where dichloroacetic acid is present, the curves deviate more from the straight line, and the "dip" before the eutectic is more pronounced. Finally, in systems containing trichloroacetic acid, the curves fall away rapidly in the neighborhood of the eutectic point

It remains to show how this difference in character is connected with the relative extent of compound formation in the mixture The freezing point of a pure substance, A, will, under normal conditions,[1] be equally

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[1] That is, provided the substance added is not *associated* or *dissociated* in the solution —It is not intended to imply, in the following discussion, that association or dissociation of the substances present in the systems considered can be entirely disregarded Organic acids, as a class, are certainly associated to some extent in the liquid state, also the conception that the addition reaction taking place in the solution is *ionic* (Kendall, THIS JOURNAL, 36, 1242 (1914)) assumes dissociation Nevertheless, the regularity of the results obtained indicates clearly that the figures given in Table I are legitimately comparable, and that the above disturbing influences are only of secondary importance.

depressed on addition of equimolecular amounts of different foreign substances, provided no chemical reaction has occurred. If, however, the addition of a second substance, B, to A is accompanied by the formation of an addition compound, AB, then the freezing point of A will be abnormally lowered, since part of the original solvent will have been replaced by a foreign substance, the compound AB. The more stable the addition product is, the greater will be the abnormal depression of the freezing point. Hence, the form of the curves obtained, when different substances are added to A, indicates the relative extent of compound formation in each case.

In the systems examined above, chloroacetic acid shows no tendency to compound formation throughout, and the freezing point curves approximate to straight lines.[1] Where dichloroacetic acid is present, on the other hand, addition products are formed and can in some cases be isolated, although they are evidently, from the flatness of their curves near the maximum point, largely dissociated into their components in the liquid state. On first addition of dichloroacetic acid to an acid in Series A, the extent of compound formation will be very small.[2] Further addition of dichloroacetic acid will increase the amount of the compound present,[3] and that this corresponds with an abnormal depression of the freezing point is indicated by the "falling away" of the curves as the eutectic is approached. Systems in which trichloroacetic acid is a component are similar in type, but the addition products formed are more stable. In accordance with this, the freezing point depression in the central part of the curve becomes still more abnormal, as is evidenced by the systems shown in Diagram I.

We are, therefore, able to discover by comparison to what extent compound formation has occurred in any particular system, from the form of the freezing-point curve alone, even if it is not possible actually to isolate the compound. This is illustrated by the figures given in Table I, where the freezing-point depressions of the acids in Series A, due to addition of equimolecular amounts of the various acids in Series B, are col-

---

[1] Where the point of fusion of the second acid of the system is very high (*e. g.*, *p*-toluic acid) a sharp final bend in the curve is necessary to enable it to reach the eutectic point at all The main portion of the curve, however, still remains linear. Compare Fig 2, Curve IV.

[2] The reversible reaction A + B $\rightleftharpoons$ AB gives the equation for equilibrium:

$$c_{AB}/c_A c_B = k$$

(*c* = molecular concentration, *k* = constant.) If the compound AB is largely dissociated on fusion, the constant *k* of the reaction will be small. Hence, when c_B is small, c_{AB} is also very small. The extent of compound formation will obviously be greatest in the central portion of the curve.

[3] Not only for the reason given in the previous note, but also since the addition products formed are more stable, the lower the temperature.

lected.   The values given are obtained directly by interpolation from the freezing-point curves.[1]   (T_{50} = freezing point of 50% mixture: Δ = depression.)

TABLE I

Acid A	Trichloroacetic		Dichloroacetic		Chloroacetic.	
	T_{50}	Δ	T_{50}	Δ	T_{50}	Δ.
Benzoic...	50 6	70 4	63 7	57 3	77 2	43 8
o-Toluic	47 2	56 2	61 6	41 8	69 8	33.6
m-Toluic....	40 4	67 2	59 4	48 2	68 8	38.8
p-Toluic.	115 2	63 4	125 2	53 4	134 1	44 5
α-Toluic	14 4	62 3	22 3	54 4	35 3	41 4
Cinnamic	68 0	68 8	77 5	59 3	90 9	45 9
Crotonic	—9 6	80 6	9 8	61 2	23 2	47.8

The above results show that, throughout the entire series, the freezing-point depression caused by trichloroacetic acid is greater than that caused by dichloroacetic acid, which is in turn greater than that caused by chloroacetic acid.

This dependence of compound formation upon difference in acidic strength is evidently in complete accordance with the views on oxonium salt formation developed in the introduction.   The regularity of the values obtained indicates that the results are not greatly influenced by any disturbing factors (association or dissociation in the solution).[2]   Further evidence on the point is to be obtained from systems containing acids of similar strengths (25–27, above).   From these we have:

TABLE II.

Original acid	Acid added	T_{50}.	Δ.
Benzoic..	α-Toluic	75 5	45 5
Benzoic ..	Cinnamic	75.6	45 4
Benzoic	Acetic	78 5	42 5
Benzoic.	Chloroacetic	77 2	43.8)
Cinnamic.... .. .	Benzoic	90 4	46 4
Cinnamic..	Chloroacetic	90 9	45 9)

Here T_{50} and Δ have the same significance as in Table I; the figures for chloroacetic acid are included for comparison.   The constancy of Δ for benzoic acid with different acids exhibiting no tendency to compound formation shows that conditions in the above systems are, if not normal, at least comparable.[3]   The freezing-point depression caused by chloro-

[1] In a few cases a short extrapolation is necessary.   The figures for acetic acid are not given, since here a longer extrapolation is required and accurate values cannot be obtained.   The curves indicate, however, that the results are qualitatively similar to those given above

[2] See note on page 1731.

[3] For small additions of B to A (up to 20%), the freezing-point curves are practically identical, whatever acid in Series B is added.   In this region the extent of compound formation is small in all cases (see Note 2, page 1732).

acetic acid is approximately normal; it is evident that its acidic strength is insufficient to suppress the acidic properties of the weaker acid of the system so far as to induce combination.

Addition reactions of the nature dealt with in this paper have been little investigated; a few compounds of the type acid—acid have been previously described[1] but not systematically examined. The similarity of the components accounts for the small number of compounds isolated in the present research, but further experiments indicate that formation of addition products is of very general occurrence in organic reactions, e. g., as an intermediate stage in condensations.[2] That this is not generally recognized is due to the neglect of the freezing-point method in the study of organic reactions.

It seems to be still the rule in experimental work to torture substances into combination by the drastic method (inherited from the alchemists) of applying *heat*. This certainly gives us the final products of a reaction (or series of reactions), but affords no clue to its mechanism. If, on the other hand, we mix the components at as low a temperature as possible and then, by *freezing* the mixture, isolate addition products, we have obtained definite knowledge of an intermediate stage of the reaction. This will be exemplified in a forthcoming paper on sulfonation.

Summary.

The freezing-point curves of a series of weak organic acids with the chloro-substituted acetic acids have been investigated. The tendency towards formation of addition compounds is found to be dependent upon the difference in acidic strengths of the two components. Acids widely divergent in strength give addition compounds which may readily be isolated.

The reaction is regarded as an oxonium salt formation, and may be expressed as follows:

$$R—C=O\pm + HX \rightleftharpoons R—C=O\underset{X}{\overset{H}{<}}$$
$$\underset{OH}{|} \qquad\qquad\qquad \underset{OH}{|}$$
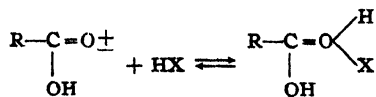
The quantitative results obtained are in complete agreement with this view.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
        COLUMBIA UNIVERSITY, NEW YORK CITY.

[1] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, 21, 353 (1902); Pfeiffer, *Ber.*, 47, 1593 (1914).

[2] Compare Guye, *J. chim. physique*, 8, 119 (1910). The view has also been advanced by Michael that an addition process represents an intermediate stage in substitution reactions (THIS JOURNAL, 32, 1001 (1910)).

RESEARCHES ON HYDANTOINS. XXVIII. THE SYNTHESIS OF 1,3,4-TRISUBSTITUTED HYDANTOINS FROM DI-ETHYL ANILINOMALONATE.

BY TREAT B JOHNSON AND NORMAN A SHEPARD
Received May 25, 1914

Hydantoin and 2 thiohydantoin interact smoothly with aromatic aldehydes[1] when heated together in acetic acid solution and in the presence of anhydrous sodium acetate, forming characteristic condensation products as represented by formulas (I) and (II), respectively

$$
\begin{array}{cc}
\text{NH—CO} & \text{NH—CO} \\
| \quad\quad | & | \quad\quad | \\
\text{CO} \quad\quad | & \text{CS} \quad\quad | \\
| \quad\quad | & | \quad\quad | \\
\text{NH—C} \quad \text{CHR} & \text{NH—C} \quad \text{CHR} \\
\text{(I)} & \text{(II)}
\end{array}
$$
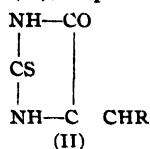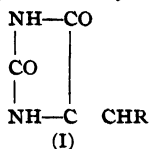
The reactions are generally very smooth and have been applied successfully in this laboratory with a great variety of aldehydes   The only types of hydantoins which have been recorded as not undergoing condensations in the above manner, are the 3-monosubstituted and 1,3-disubstituted hydantoins   Wheeler and Hoffmann[2] observed, for example, that neither 3-phenyl- nor 1,3-diphenylhydantoins (III and IV)

$$
\begin{array}{cc}
\text{NH—CO} & \text{C}_6\text{H}_5\text{N—CO} \\
| \quad\quad | & | \quad\quad | \\
\text{(S)CO} \quad\quad | & \text{(S)CO} \quad\quad | \\
| \quad\quad | & | \quad\quad | \\
\text{C}_6\text{H}_5\,\text{N——CH}_2 & \text{C}_6\text{H}_5\text{N—CH}_2 \\
\text{(III)} & \text{(IV)}
\end{array}
$$
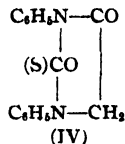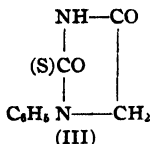
condense with anisic aldehyde in the presence of sodium acetate and acetic anhydride   On the other hand, the corresponding 2-thiohydantoins were later observed to condense smoothly with aldehydes, giving good yields of condensation products.[3] It is also of especial interest to note here, at this time, that Biltz[4] has recorded an observation that 1,3-dimethylhydantoin (V) does not condense with benzaldehyde. Whether this abnormal behavior is to be explained by the fact that such hydan-

$$
\begin{array}{cc}
\text{CH}_3\text{N — CO} & \text{CH}_3\text{N—C OH} \\
| \quad\quad | & | \quad\quad \| \\
\text{CO} \quad\quad | & \text{CO} \quad\quad \| \\
| \quad\quad | & | \quad\quad \| \\
\text{CH}_3\text{N—CH}_2 & \text{CH}_3\text{N—CH} \\
\text{(V)} & \text{(VI)}
\end{array}
$$
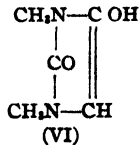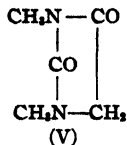
[1] The behavior of aliphatic aldehydes towards hydantoins is now being investigated in this laboratory (T B J)

[2] *Am Chem J* , **45,** 368 (1911)

[3] Wheeler and Brautlecht, *Am Chem J* , **45,** 446 (1911)

[4] *Ber* , **45,** 1673 (1911)

toins have not a normal constitution (V), but are to be expressed by their pseudo or enol form (VI), must be decided by further investigation.

The study of several of these abnormal cases is now being continued in this laboratory. During the progress of this work, important and unexpected experimental data were obtained,[1] which has made it necessary to develop a new method of preparing trisubstituted hydantoins of the types represented by 1,3-diphenyl-4-benzylhydantoin and its corresponding sulfur analog (Formulas XII and XIV). In other words, it was necessary to have available a practical method of synthesis which does not involve the condensation of an aldehyde with a hydantoin and, furthermore, be applicable for the preparation of any alkylhydantoin desirable, with substituents in the 1,3 and 4 positions of the ring. A description of a method of synthesis, which meets all these requirements, and of its application for the preparation of the hydantoins (XII) and (XIV) is now recorded in this paper.

That diethyl anilinomalonate reacts at ordinary temperature, with alcoholic sodium ethylate, giving a sodium salt, was first obser'ure by Curtiss.[2] No data indicating that he investigated the chemical activity of this substance are recorded, however, in his paper. Later Conrad and Reinbach,[3] who were working with dimethyl anilinomalonate, made the interesting observation that the sodium salt of this ester interacts smoothly with alkyl halides, forming the corresponding substituted anilino malonates. They prepared, in this manner, the following amino esters: dimethyl methylanilinomalonate, $C_6H_5NH(CH_3)C(COOCH_3)_2$, dimethyl benzylanilinomalonate, $C_6H_5NH(C_6H_5CH_2)C(COOCH_3)_2$, dimethyl o-nitrobenzylanilinomalonate, $C_6H_5NH(NO_2.C_6H_4CH_2)C(COOCH_3)_2$, and trimethyl anilinoethantricarboxylate, $C_6H_5NH.(CH_2COOCH_3)C(COOCH_3)_2$. Recently, Johnson and Shepard[4] investigated the action of p-nitrobenzyl chloride on the sodium salt of diethyl anilinomalonate and obtained the corresponding ester, $C_6H_5NH(NO_2C_6H_4CH_2)C.(COOC_2H_5)_2$. As a by-product of this reaction, they also succeeded in isolating a crystalline substance to which they provisionally assigned the constitution of α-nitrobenzylindoxyl.

The starting point of this investigation was the diethyl ester of benzylanilinomalonate (VIII). This was obtained easily by the action of benzylchloride on the sodium salt of diethylanilinomalonate. The reaction was very smooth, and, to our surprise, we did not observe the formation of α-benzylindoxyl (X). This ester (VIII) was converted into the corresponding acid (XI) by saponification, and the latter transformed into α-anilino-β-phenylpropionic acid (XIII) by heating above its melting

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[1] The results of this investigation, which is being conducted by Mr. Sidney Hadley, will be discussed in a future paper (T. B. J.).

[2] Am. Chem. J., 19, 694 (1885).

[3] Ber., 35, 511 (1903).

[4] THIS JOURNAL, 35, 994 (1913).

point. We found, however, that this change is best effected by boiling an alcoholic solution of the malonic acid, when an almost quantitative yield of the monobasic acid (XIII) is obtained. This observation is of special interest because of the low temperature at which the dissociation of the malonic acid is effected, namely, nearly 100° lower than that temperature at which the acid is decomposed by direct heating.

The acid (XIII) interacts with both phenylisothiocyanate and phenylisocyanate, when heated with it at 130–140°, giving hydantoin compounds. In the first case 1,3-diphenyl-4-benzyl-2-thiohydantoin (XII) is formed in good yield. Phenylisocyanate, however, reacts far less smoothly with the anilino acid, forming 1,3-diphenyl-4-benzylhydantoin (XIV). The latter hydantoin is also formed by desulfurization of the thiohydantoin (XII) This is easily accomplished by heating the sulfur hydantoin under pressure with a strong aqueous solution of chloroacetic acid. As a by-product of the above reactions with phenylisothiocyanate and phenylcyanate, we obtained a crystalline substance which gave analytical v$_{this}$ s agreeing for α-benzylindoxyl (X). 1,3-Diphenyl-4-benzyl-2-thionyhydantoin melts at 129–130°. The corresponding oxygen derivative was, however, always obtained as an oil which solidified only after long standing. These various changes are represented ⱶ the following formulas·

C₆H₅NH CH(COOC₂H₅)₂
(VII)

C₆H₅CH₂
        >C(COOC₂H₅)₂
C₆H₅NH
        (VIII)

NH—CO
| | CH₂C₆H₅
CS   C
| | NHC₆H₅
NH—CO
(IX)

CO
   >CH CH₂C₆H₅
NH
(X)

C₆H₅CH₂
        >C(COOH)₂
C₆H₅NH
        (XI)

C₆H₅N—CO
|
CS |
|
C₆H₅N—CHCH₂C₆H₅
(XII)

C₆H₅NCS C₆H₅CH₂CH(NHC₆H₅)COOH
(XIII)

C₆H₅NCO

C₆H₅N—CO
|
CO |
|
C₆H₅N—CH.CH₂C₆H₅
(XIV)
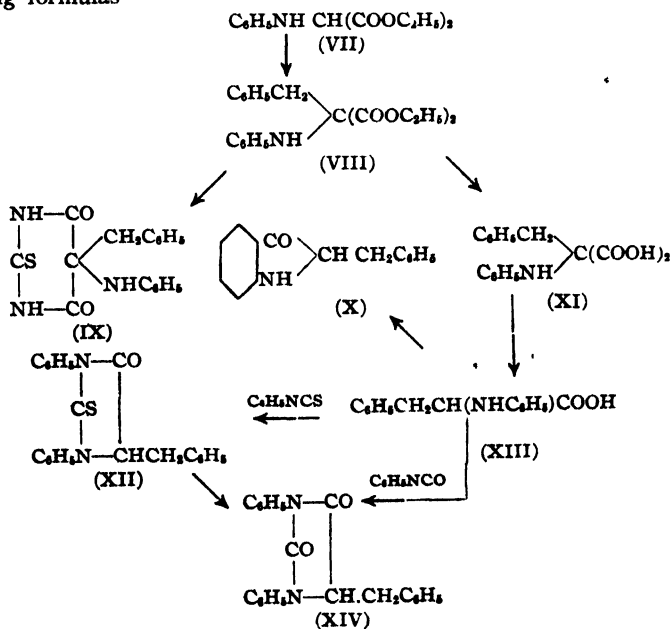
This new method of synthesis will be applied for the preparation of new types of hydantoins which have hitherto received no attention.

Diethyl anilinomalonate, diethylphthalimidomalonate,[1] and diethylaminomalonate,[2] all condense with thiourea, in the presence of sodium ethylate, giving thiouranils. Benzylanilinomalonate (VIII) interacts in an analogous manner, forming 5,5-benzylanilino-2-thiobarbituric acid (IX).

Experimental Part.

Diethylbenzylanilinomalonate, $\underset{C_6H_5NH}{\overset{C_6H_5CH_2}{>}}C(COOC_2H_5)_2$ —This ester was prepared by the action of benzylchloride on the sodium salt of diethyl anilinomalonate. Three and six-tenths grams of sodium were dissolved in 200 cc. of absolute alcohol and 40 grams of the diethyl ester added to the solution. On warming gently, the ester dissolved, and finally its sodium salt began to deposit. Twenty and four-tenths grams of freshly distilled benzylchloride were then added and the mixture heated on the steam bath. There was an immediate reaction with separation of sodium chloride and within a few minutes the reaction was complete. The alcohol was then removed by distillation under diminished pressure, when the aniline ester was obtained as a heavy yellow oil. This was washed with water to remove sodium chloride, extracted with ether and dried over potassium carbonate. We obtained 50 g. of the crude, dry ester, corresponding to a yield of 93% of the theoretical. It was found that this ester can be distilled under diminished pressure, but not without considerable decomposition. It boiled at 257–260° at 50 mm. For our investigation, however, it was used without further purification.

Potassium Salt of Benzylanilinomalonic Acid, $\underset{C_6H_5NH}{\overset{C_6H_5CH_2}{>}}C(COOK)_2$.— Fifty grams of the crude diethyl ester (above) were saponified by heating with 24.6 g. of potassium hydroxide in 56 cc. of 50% alcohol. The potassium salt soon began to separate. After heating for 2 hrs. the solution was cooled to 0° and the salt separated by filtration. It was purified by crystallization from 50% alcohol and deposited in beautiful, colorless, hexagonal plates. When heated at 295–300° for a long time it finally melted to a clear yellow oil. The yield of purified salt was 28 g.

Calc. for $C_{16}H_{13}O_4NK_2$: N, 3.88; found: N, 3 84, 4.1.

From the alcohol filtrates left after purification of this salt, we isolated 4.5 g. of α-anilino-β-phenylpropionic acid (see below). This corresponds to 6.7 g. of the dipotassium salt of benzylanilinomalonate.

[1] Johnson and Shepard, *Loc. cit.*
[2] Johnson and Nicolet, THIS JOURNAL, 36 (1914).

Benzylanilinomalonic Acid, $\begin{array}{c} C_6H_5CH_2 \\ \diagdown \\ \diagup \\ C_6H_5NH \end{array}$ $C(COOH)_2$.—A quantitative yield of this acid was obtained by treatment of the above potassium salt in aqueous solution with hydrochloric acid. All attempts to purify the acid by crystallization from alcohol were unsuccessful, as carbon dioxide was evolved immediately on warming the solutions. It was purified for analysis by precipitation with hydrochloric acid from an ice-cold solution of its potassium salt. Under these conditions it separated in clusters of radiating needles, which melted at 170 173° to a clear oil. Carbon dioxide was evolved when the acid was heated to 190 200°.

Calc. for $C_{16}H_{15}O_4N$. N, 4.91; found: N, 4.87, 5.07.

Disilver Salt.—This was obtained by dissolving the potassium salt in water and then adding the required amount of silver nitrate. It separated as a colorless, amorphous precipitate, which was unstable on heating. Analysis of the salt after drying in a desiccator over concentrated sulfuric acid:

Calc. for $C_{16}H_{13}O_4NAg_2$: N, 2.8; found. N, 2.78.

α-Anilino-β-phenylpropionic Acid, $C_6H_5CH_2CH(NHC_6H_5)COOH$.—Benzylanilinomalonic acid readily loses carbon dioxide when heated above its melting point and is converted into this amino acid. Much decomposition, however, takes place by this treatment and the yield is not good. It is best prepared by heating an alcoholic solution (absolute or dilute) of the malonic acid at the boiling temperature for a few minutes. On cooling, the propionic acid separates in glistening plates showing distinct, rhombic forms. This compound begins to yield at 165°, when heated in a capillary tube, and then melts at 170-3° to a clear oil without any apparent decomposition. It is easily soluble in alcohol, moderately soluble in benzene, and cold ether, and difficultly soluble in hot water. It is best purified by recrystallization from 50% alcohol.

Calc. for $C_{15}H_{15}O_2N$: N, 5.8; found: N, 5.88, 5.99, 6.06.

Ethyl Ester, $C_{17}H_{19}O_2N$.—This is easily obtained, in the usual manner, by esterification of the acid with ethyl alcohol in the presence of sulfuric acid. After removing the excess of alcohol, by heating under diminished pressure, the ester was extracted with ether, washed with water, and finally dried over anhydrous sodium sulfate. It was purified by distillation under diminished pressure and boiled at 206-9° at 12 mm. A second sample boiled at 218-221° at 19 mm. pressure. Under these conditions the ester was obtained as a thick, yellow oil, which solidified on standing. It crystallized from alcohol in stout, hexagonal prisms or blocks which melted at 48-49° to a clear oil without decomposition. The weight of purified material was 5.0 g. or 68% of a theoretical yield.

Calc. for $C_{17}H_{19}O_2N$: N, 5.20; found: N, 5.18, 5.15.

7,3-Diphenyl-2-thio-4-benzylhydantoin,

$$C_4H_5N—CO$$
$$CS$$
$$C_4H_5N—CHCH_2C_4H_5$$
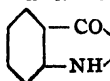
.—Three and four-tenths grams of α-anilino-β-phenylpropionic acid and 1.9 g. of phenyl mustard oil were heated together at 130–135°. Water was evolved immediately, and a small amount of the unchanged propionic acid sublimed during the operation. After heating for 5 hrs. we obtained a brown oil, which was diluted with alcohol. A crystalline substance separated at once. This was separated and then triturated with cold benzene, when the above hydantoin dissolved, immediately leaving behind an insoluble crystalline product (see below).

The benzene solution was evaporated, whereupon we obtained a yellow gum which immediately solidified after trituration with 95% alcohol. This was purified by crystallization from alcohol and separated in clusters of needle-like prisms which melted at 129–130° to a clear oil without decomposition. The hydantoin gave a strong test for sulfur. The compound is very soluble in cold benzene and ether; easily soluble in glacial acetic acid, and very difficultly soluble in hot water. It is insoluble in dilute sodium hydroxide solution even on warming. The yield of purified material was 56% of the theoretical.

Calc. for $C_{22}H_{18}ON_2S$: N, 7.82; found: N, 7.96, 7.94.

α-*Benzylindoxyl*,

in the preceding experiment, which was insoluble in cold benzene, was purified by crystallization from glacial acetic acid. It separated in well-defined, prismatic crystals (cubical) which melted at 271–272° to a clear oil. They did not contain sulfur. The compound was difficultly soluble in water and very soluble in alcohol and acetic acid. The yield was very small.

Calc. for $C_{15}H_{13}ON$: N, 6.28; found: N, 6.21

Several attempts were made to obtain this compound in larger quantities. The corresponding *p*-nitrobenzyl derivative[1] was obtained as a secondary product in the preparation of diethyl nitrobenzylanilinomalonate, and it seemed probable that this corresponding benzyl compound would be formed under similar conditions. A careful examination, however, of the secondary products formed in the reaction between benzyl chloride and the sodium salt of diethyl anilinomalonate failed to reveal a trace of the indoxyl compound.

Benzylanilinomalonic acid was also heated with phenylisothiocyanate, but, here again, the yield of indoxyl was not increased. This malonic

[1] Johnson and Shepard, *Loc. cit.*

acid was also heated alone at its melting point, but no formation of the indoxyl compound was observed. We finally heated α-anilino-β-phenyl-propionic acid with potassium hydroxide at 200°, but the result was negative, nothing but benzoic acid being identified.   '

$C_6H_5N—CO$

1,3-Diphenyl-4-benzylhydantoin, $\begin{array}{c} CO \\ | \\ C_6H_5N—CHCH_2C_6H_5 \end{array}$.—This hydantoin
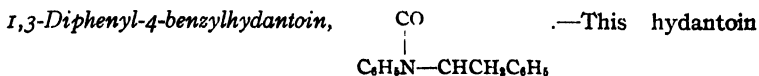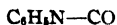
is formed by the action of phenylisocyanate on α-anilino-β-phenyl-propionic acid. The reaction, however, is not smooth and the yield of hydantoin is poor. One and three-tenths grams of the propionic acid were heated with 0.8 g. of the isocyanate for 3 hrs. at 140–150°, when a brown colored product was obtained. On triturating with alcohol, the latter completely dissolved with the exception of a very small amount of crystalline material, which melted at 270-272°. This was α-benzyl-indoxyl. The alcohol filtrate was concentrated to remove the alcohol, when an oil was obtained which dissolved in ether. A small amount of diphenylurea was obtained by this treatment. After drying the ether and then allowing to evaporate the diphenylhydantoin was obtained as an oil which finally solidified after long standing. This hydantoin is extremely soluble in the common organic solvents and was not obtained in a crystalline condition. The crude dry product melted from 58 to 62°

Calc. for $C_{22}H_{18}O_2N$: N, 8.1; found (Kjeldahl): N, 7.75.

This same hydantoin is also formed by heating phenylisocyanate with the ethyl ester of α-anilino-β-phenylpropionic acid.

· *Formation of 1,3-Diphenyl-4-benzylhydantoin by Desulfurization of 1,3-Diphenyl-2-thio-4-benzylhydantoin.*—Three grams of the thiohydantoin were heated with 8.0 g. of chloroacetic acid and 15 cc. of water for 6 hours at 150°. The desulfurized product was obtained as an oil. This was finally digested with hydrochloric acid to destroy any addition product formed with the halogen acid and then dissolved in ether and dried over calcium chloride. After evaporating the ether the hydantoin was then dried over concentrated sulfuric acid and finally by heating at 105–110°.

Calc. for $C_{22}H_{18}O_2N_2$: N, 8.1; found: N, 7.72.

2-Thio-5-benzyl-7-phenyluramil, $\begin{array}{c} NH—CO \\ | \quad | \quad \diagup CH_2C_6H_5 \\ CS \quad C \\ | \quad | \quad \diagdown NH.C_6H_5 \\ NH—CO \end{array}$.—This uramil was
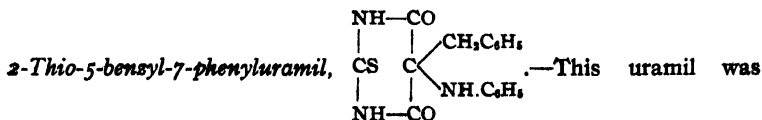
obtained in the form of its sodium salt by digesting thiourea in alcoholic solution with sodium ethylate (2 molecular proportions) and diethyl benzylanilinomalonate. After heating on the steam bath for 9 hrs. the yellow sodium salt, which had deposited, was separated by filtration and

dissolved in water. After washing with ether to remove a trace of oil, the uramil was precipitated by addition of hydrochloric acid. It separated as an oil, which finally solidified on standing. The yield was 2.1 g. or 35% of theory. It was purified by crystallization from alcohol and separated in stout, prismatic blocks. They melted at 219–220° to a clear oil, which soon began to decompose with effervescence. This pyrimidine is very soluble in glacial acetic acid, moderately soluble in hot benzene and cold ether, and very difficultly soluble in hot water. The condensation was repeated with four molecular proportions of sodium, but the yield of pyrimidine was not increased. A portion of the malonic ester undergoes decomposition during the reaction and α-anilino-β-phenylpropionic acid is formed.

Calc. for $C_{17}H_{15}O_2N_3S$: N, 12.92; found: N, 12.75, 12.69, 13.03.

NEW HAVEN, CONN
May 20, 1914.

RESEARCHES ON PYRIMIDINES: LXXI. SYNTHESIS OF THE PYRIMIDINE NUCLEOSIDE, 4-HYDROXYMETHYLURACIL.

BY TREAT B. JOHNSON AND LEWIS H CHERNOFF.
Received June 6, 1914.

This paper is our third contribution to the chemistry of pyrimidine nucleosides.[1] It includes a description of the synthesis and properties of the simple nucleoside of uracil, namely, *2,6-dioxy-4-hydroxymethylpyrimidine* represented by Formula (I).
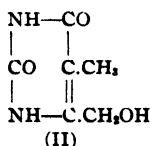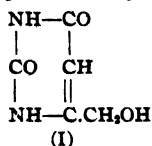
The method of synthesis, which has been applied successfully for the preparation of this interesting pyrimidine, is perfectly analogous to that employed for the preparation of the corresponding simple nucleoside of thymine, namely, 2,6-dioxy-4-hydroxymethyl-5-methylpyrimidine[2] represented by Formula (II). The starting point, in this case, was the ethyl ester of ethoxyacetic acid (III), which was prepared in quantity by interaction of sodium ethylate with ethyl chloroacetate, and also from the nitrile $C_2H_5O.CH_2CN$[3] by direct esterification with ethyl alcohol in the presence of hydrochloric acid (imidoester method). The ester undergoes condensation with ethyl bromoacetate, in the presence of amalgamated

[1] Johnson and Chernoff, *J. Biol. Chem.*, 14, 307; THIS JOURNAL, 35, 585 (1913).
[2] Johnson and Chernoff, *Loc cit.*
[3] Sommelet, *Compt. rend.*, 143, 827.

zinc,[1] giving the β-ketone ester—*ethyl γ-ethoxyacetoacetate* (IV)   The reaction may be expressed by the following equation [2]

$C_2H_5OCH_2COOC_2H_5 + Zn Hg + Br CH_2 COOC_2H_5 =$
(III)

$$C_2H_5OCH_2C \overset{OC_2H_5}{\underset{OZnBr}{-\!\!\!-}} CH_2COOC_2H_5 \xrightarrow{H_2O}$$

$$C_2H_5OH + Zn(OH)Br + C_2H_5O CH_2 COCH_2COOC_2H_5$$
(IV)
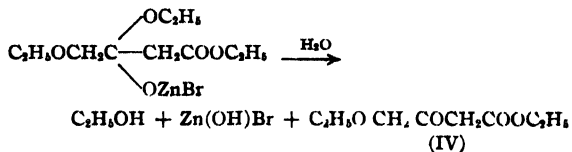
This ester (IV) exhibits the normal properties of a β-ketone ester and condenses normally with thiourea in alcoholic solution and in the presence of sodium ethylate, forming the sodium salt of the thiopyrimidine represented by Formula (V)   The yield of this pyrimidine was excellent. The condensation may be represented as follows

$$\begin{array}{ccc} NH_2 & COOC_2H_5 & NH-CO \\ | & | & | \quad | \\ CS & + CH_2 & = CS \quad CH & + H_2O + C_2H_5OH \\ | & | & | \quad || \\ NH_2 & CO CH_2OC_2H_5 & NH-C CH_2OC_2H_5 \end{array}$$
(V)
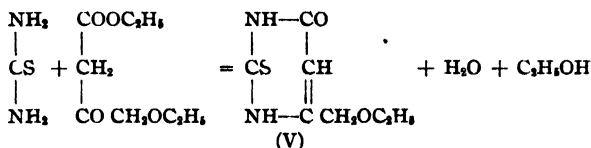
Little difficulty was encountered in converting quantitatively this thiopyrimidine (V), into its corresponding oxygen derivative (VI)   This was accomplished by digesting the thiopyrimidine, in aqueous solution, with chloroacetic acid.   The mechanism of this change may be represented by the following formulas

$$\begin{array}{ccc} NH-CO & & NH-CO \\ | \quad | & \xrightarrow{ClCH_2COOH} & HOOC CH_2 \quad | \quad | \\ CS \quad CH & & \quad\quad S = C \quad CH \\ | \quad || & & Cl \quad | \quad || \\ NH-C CH_2OC_2H_5 & & NH-C CH_2OC_2H_5 \end{array} \longrightarrow$$

$$\begin{array}{ccc} NH-CO & & NH-CO \\ HOOCCH_2S-C \quad CH & \xrightarrow[HCl]{H_2O} & HSCH_2COOH + CO \quad CH \\ || \quad || & & \cdot \quad | \quad || \\ N-C CH_2OC_2H_5 & & NH-C CH_2OC_2H_5 \end{array}$$
(VI)
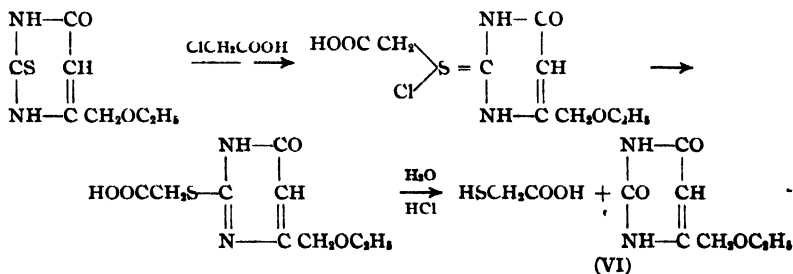
4-Ethoxymethyluracil (VI) is very stable in the presence of acids. It undergoes no change when heated with 10% sulfuric acid at 140°. When heated with concentrated hydrochloric acid at 100°, ethyl chloride

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[1] Johnson, THIS JOURNAL, **35,** 582 (1913)

[2] This reaction has been applied successfully with a number of other esters and the interesting results, which have been obtained, will be discussed in future papers   These types of β-ketone have hitherto received practically no attention, and should be of value for the synthesis of other important combinations of immediate biochemical and therapeutic interest   (T B Johnson)

was evolved and the pyrimidine ether was converted smoothly into the primary halide, 2,6-dioxy-4-chloromethylpyrimidine (VII).

$$
\begin{array}{ccc}
\text{NH—CO} & \text{NH—CO} & \text{NH—CO} \\
|\quad\quad| & |\quad\quad| & |\quad\quad| \\
\text{CO}\quad\text{CH} \xrightarrow{\text{HCl}} & \text{CO}\quad\text{CH} \xrightarrow{\text{HCl}} & \text{CO}\quad\text{CH} \\
|\quad\quad\| & |\quad\quad\| & |\quad\quad\| \\
\text{NH—C.CH}_2\text{OC}_2\text{H}_4 & \text{NH—CCH}_2\text{OH} & \text{NH—C.CH}_2\text{Cl} \\
& & \text{(VII)}
\end{array}
$$
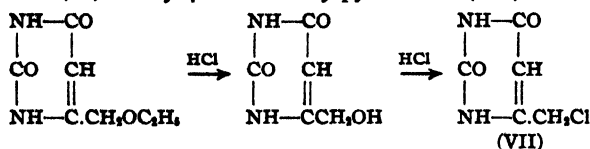
In order to convert this chloropyrimidine (VII), into the simple nucleoside of uracil (I), it was first digested in aqueous solution, with silver sulfate to remove the halogen and the resulting sulfate was then decomposed by digesting with an aqueous solution of barium hydroxide. In this manner, the nucleoside (I) was easily obtained in a colorless, crystalline condition. A description of this compound is given in the experimental part of this paper.

$$
\begin{array}{cccc}
\text{NH—CO} & & \left(\text{NH—CO}\right) & \text{NH—CO} \\
|\quad\quad| & & |\quad\quad| & |\quad\quad| \\
2\ \text{CO}\quad\text{CH} + \text{Ag}_2\text{SO}_4 \longrightarrow & & \left(\text{CO}\quad\text{CH}\right)\text{SO}_2 \xrightarrow{\text{Ba(OH)}_2} & \text{CO}\quad\text{CH} \\
|\quad\quad\| & & |\quad\quad\| & |\quad\quad\| \\
\text{NH—C.CH}_2\text{Cl} & & \left(\text{NH—C.CH}_2\text{O}\right)_2 & \text{NH—C CH}_2\text{OH} \\
& & & \text{(I)}
\end{array}
$$
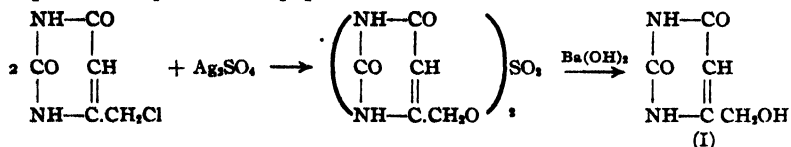
The structures of the ethers (V) and (VI), the halide (VII), and the nucleoside (I), were all established by the behavior of the uracilnucleoside on reduction. When digested in hydriodic acid solution, in the presence of a small amount of phosphorus, it underwent reduction smoothly and was converted into Behrend's 4-methyluracil (VIII).

$$
\begin{array}{cc}
\text{NH—CO} & \text{NH—CO} \\
|\quad\quad| & |\quad\quad| \\
\text{CO}\quad\text{CH} + 2\text{HI} = & \text{CO}\quad\text{CH} + \text{I}_2 + \text{H}_2\text{O} \\
|\quad\quad\| & |\quad\quad\| \\
\text{NH—C.CH}_2\text{OH} & \text{NH—C.CH}_3 \\
\text{(VIII)} &
\end{array}
$$
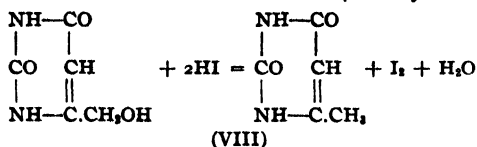
Experimental Part.

Ethyl γ-Ethoxyacetoacetate, $C_2H_5OCH_2CO.CH_2COOC_2H_5$.—The boiling point of this ester has previously been recorded in a paper from this laboratory.[1] The ester is easily obtained by interaction of molecular proportions of ethyl ethoxyacetate and ethyl bromoacetate in the presence of amalgamated zinc. The esters were mixed with one or two molecular proportions of amalgamated zinc, in a dry flask connected to a reflux condenser, and the mixture then warmed on a steam bath. At first, there was no apparent evidence of a reaction, but, on continued warming, there was finally a great evolution of heat and the reaction became so violent that it was necessary to cool with ice water. Within a few minutes, however, the violent reaction was over and the mixture was then heated

[1] Johnson, *loc. cit.*

at 100° for 10 hours. We obtained a dark colored syrupy product, which was poured into cold water to decompose the double zinc compound. After acidifying with hydrochloric acid, to complete the decomposition and to dissolve the zinc hydroxide, the oil was thoroughly extracted with ether and the acid filtrate discarded. The ether solution of the crude oil was then washed several times with cold, dilute sodium hydroxide solution in order to remove the β-ketone ester. On acidifying this alkaline solution with hydrochloric acid (cold) the ketone ester separated at once and was dissolved in ether. After washing with water and finally drying over anhydrous calcium chloride, it was then purified by distillation under diminished pressure. Some of the observed boiling points of different preparations are recorded below:

Pressure in mm	22	26	30	30	32	52
Boiling point	113°	116–120°	120–125°	117°	121°	132°

The average yield obtained was about 15% of the theoretical. The ketone ester can also be obtained by applying the condensation with ethyl chloroacetate, but the yield is smaller.

$$\begin{array}{c} NH{-}CO \\ | \quad\quad | \\ CS \quad CH \\ | \quad\quad || \\ NH{-}CCH_2OC_2H_5 \end{array}$$
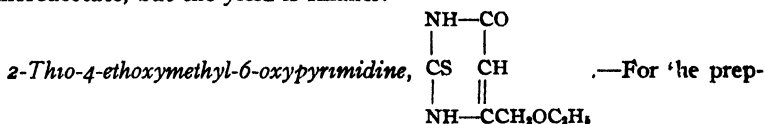
2-Thio-4-ethoxymethyl-6-oxypyrimidine, .—For 'he preparation of this new pyrimidine, molecular proportions of thiourea were condensed with ethyl γ-ethoxyacetoacetate in the presence of sodium ethylate. The quantities of reagents used in one experiment were as follows. 13.5 g. of the ketone ester, 5.9 g. of thiourea and 3.6 g. of metallic sodium The sodium was dissolved in 50 cc. of absolute alcohol and, after cooling, the thiourea and ketone ester added. The mixture was then digested on the steam bath for 7 hrs. to complete the reaction and the alcohol finally removed by evaporation on a water bath We obtained the sodium salt of the pyrimidine as a colorless solid, which was very soluble in water. On acidifying this solution with acetic acid the pyrimidine separated as a heavy crystalline precipitate. This was separated by filtration, washed with water and finally purified by crystallization from hot water. It deposited in large radiating prisms, which melted at 180–1° to a clear oil. The yield was 7.1 g.

Calc. for $C_7H_{10}O_2N_2S$· N, 15.05. Found: N, 15.07

$$\begin{array}{c} NH{-}CO \\ | \quad\quad | \\ CO \quad CH \\ | \quad\quad || \\ NH{-}C.CH_2OC_2H_5 \end{array}$$
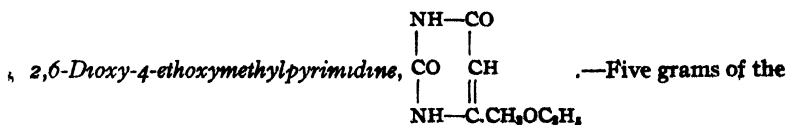
, *2,6-Dioxy-4-ethoxymethylpyrimidine*, .—Five grams of the preceding 2-thiopyrimidine and 5 g. of chloroacetic acid were dissolved in hot water (50–75 cc.) and the solution boiled for 3 hrs. when the de-

sulfurization of the thiopyrimidine was apparently complete. The mixture was then evaporated on the steam bath and the residue obtained finally triturated with cold water. The above pyrimidine was obtained in crystalline condition by this treatment. It was washed with cold water and finally purified by crystallization from hot alcohol. It separated in rhombic prisms which melted at 175° to an oil. The yield of purified pyrimidine was 2.5 g.

Calc. for $C_7H_{10}O_2N_2$: N, 16.47. Found: N, 16.44.

Behavior of 2,6-Dioxy-4-ethoxymethylpyrimidine when heated with Sulfuric Acid.—One gram of the pyrimidine and 25 cc. of 10% sulfuric acid were heated in a bomb tube for 3 hrs. at 125°. On cooling, the pyrimidine crystallized out apparently unaltered. The heating was continued for 3 hrs. at 140°, and the sulfuric acid then removed from the solution by precipitation as barium sulfate. After filtering off the sulfate, the neutral solution was concentrated and cooled, when the unaltered pyrimidine separated in the form of prismatic crystals. It melted at 174°. The pyrimidine, therefore, did not undergo conversion to uracil.
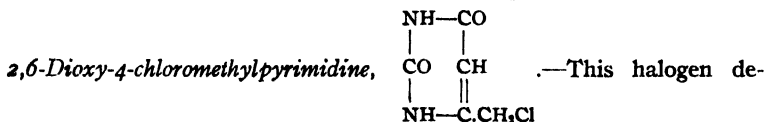
2,6-Dioxy-4-chloromethylpyrimidine,
$$\begin{array}{l} NH{-}CO \\ \mid \quad\ \mid \\ CO \quad CH \\ \mid \quad\ \parallel \\ NH{-}C.CH_2Cl \end{array}$$
.—This halogen derivative was formed by interaction of the above ethoxypyrimidine with hydrochloric acid. Two grams of the pyrimidine were heated with 50 cc. of concentrated hydrochloric acid for about 24 hrs. at 100°. The contents of the tube were then transferred to a beaker and evaporated to dryness at 100°, when a dark colored residue was obtained. This was dissolved in hot water, the solution decolorized by digesting with bone-coal and finally concentrated again to a small volume. On cooling, the chloropyrimidine finally separated in the form of small radiating prisms, which decomposed at 204–215°, depending on the rate of heating. The dust from this compound irritates the membranes of the nose producing sneezing.

Calc. for $C_5H_5O_2N_2Cl$: N, 17.45. Found: N, 17.7.

2,6-Dioxy-4-hydroxymethylpyrimidine,
$$\begin{array}{l} NH{-}CO \\ \mid \quad\ \mid \\ CO \quad CH \\ \mid \quad\ \parallel \\ NH{-}C.CH_2OH \end{array}$$
.—In order to obtain this simple nucleoside of uracil we proceeded as follows: to an aqueous solution of the above chloropyrimidine (1.4 g. in 200 cc. of water) was added an excess of silver sulfate (2.5 g.) and the mixture boiled in an open dish for about one hour, keeping the volume constant by addition of water. The insoluble silver chloride was then filtered off and the excess

of silver in solution precipitated as sulfide by hydrogen sulfide. The solution was then boiled to remove all free hydrogen sulfide and the silver sulfide separated by filtration. The sulfuric acid was then separated by precipitation as sulfate with barium hydroxide and the excess of barium precipitated as carbonate by saturating the solution with carbon dioxide. The neutral solution was then concentrated and cooled, when the nucleoside separated in prismatic crystals. This pyrimidine was purified for analysis by crystallization from hot water and separated on cooling, in small plates. They did not possess a sharp melting point. On heating in a capillary tube the pyrimidine began to show signs of melting at about 240° and then decomposed quite sharply a 254°. This decomposition point varies according to the rate of heating. The yield of purified nucleoside was 0.6 g.

Calc. for $C_6H_6O_2N_2$: N, 19.72. Found: N, 19.42.

The structure of this nucleoside was established by its behavior on reduction with hydriodic acid.

The Formation of 4-Methyluracil,

$$\begin{array}{c} NH\!-\!CO \\ |\qquad| \\ CO\quad CH \\ |\qquad\| \\ NH\!-\!C.CH_3 \end{array}$$

.—Five-tenths of a gram
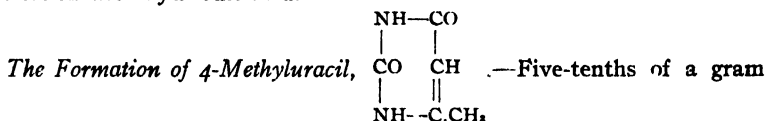
of the nucleoside was dissolved in 15 cc. of hydriodic acid (sp. gr. 1.7) and about 0.1 g. red phosphorus added to the solution. The solution was then boiled for 4 hrs., diluted with water and finally filtered to remove the phosphorus. The halogen and phosphate radicals were then removed by digesting with an excess of silver carbonate. After filtering, the excess of silver was then precipitated as sulfide with hydrogen sulfide and the aqueous solution then decolorized by boiling with bone-coal. The solution was then concentrated and cooled, when 4-methyluracil deposited in colorless crystals. It was purified by recrystallization from hot water. It did not melt or undergo decomposition below 300° and when mixed with pure 4-methyluracil this behavior, on heating, was not altered.

Calc. for $C_5H_6O_2N_2$: N, 22.22. Found: N, 21.9.

NEW HAVEN, CONN.

THE ACTION OF MONOCHLOROACETIC ACID ON SEMI-CARBAZIDE AND HYDRAZINE.

BY J. R. BAILEY AND W. T. READ.

Introduction.

Hydrazine derivatives have been prepared by the action of monochloroacetic acid on phenylhydrazine,[1] and on hydrazine,[2] but no inves-

[1] *Ber.*, **28**, 1231 (1895); **36**, 3887 (1903).

[2] *J. prakt. Chem.*, [2] **83**, 249 (1861).

tigation of a similar reaction has been published between semicarbazide and halogen acids. Our work on this latter reaction has shown that both semicarbazinoacetic acid, $NH_2CONHNHCH_2COOH$, and semicarbazino-diacetic acid, $NH_2CONHN(CH_2COOH)_2$, result when potassium chloro-acetate and semicarbazide are heated in aqueous solution. The yield of semicarbazinoacetic acid, as obtained by us, is poor, but semicarbazino-diacetic acid is readily prepared by this method. It was observed that monochloroacetic acid reacts much more easily with semicarbazide than do the halogen derivatives of the higher fatty acids, a behavior wherein semicarbazide resembles hydroxylamine.[1]

The study of the action of potassium chloroacetate on semicarbazide suggested a modification of the method of Curtius and Hussong[2] for obtaining hydrazinodiacetic acid, which has led to a simplification of their process with a greatly increased yield. This interesting substance is now available in any amount desired with a few hours' work. Curtius and Hussong employed 5 mols of hydrazine hydrate to 2 mols of monochloro-acetic acid, whereas in reality the molecule of hydrazinodiacetic acid is built from one molecule of hydrazine and two molecules of monochloro-acetic acid. In their process, one molecule of this excess of hydrazine reacts to neutralize the hydrochloric acid liberated in the reaction, and a second molecule gives with the hydrazinodiacetic acid formed a hydra-zine salt. The reactions that take place in the process may be interpreted as follows: $5NH_2NH_2 + 2CH_2ClCOOH = NH_2N(CH_2COOH)_2.NH_2NH_2 + NH_2NH_2.2HCl + 2NH_2NH_2$ excess. The excess hydrazine, as well as the hydrazine forming a salt with the hydrazinodiacetic acid, is removed here by fractional precipitation with benzaldehyde. Hydrazinodiacetic acid itself does not react with aldehydes. It is simply freed from the hydrazine salt by the action of the aldehyde and separates along with benzalazine, and the latter is removed by alcohol. In the modification of this process, as worked out by us, 1 mol of hydrazine hydrate, 2 mols of $CH_2ClCOOH$ and 2 mols of K_2CO_3 are employed, the reaction proceeding as follows:

$$NH_2NH_2 + 2CH_2ClCOOH + 2K_2CO_3 = NH_2N(CH_2COOK)_2 + 2KCl + 2CO_2 + 2H_2O.$$

At the end of the reaction, the hydrazinodiacetic acid is liberated from its salt by neutralization with hydrochloric acid, whereupon the hydrazine acid crystallizes out. This method is similar to the one employed by M. Busch in the preparation of asymmetric phenylhydrazinoacetic acid, $C_6H_5N(CH_2COOH)NH_2$, from 1 mol phenylhydrazine, 1 mol monochloro-acetic acid, and 1 mol potassium carbonate.[3] Curtius obtained from 50

[1] *Ann.*, 289, 285 (1896).

[2] *J. prakt. Chem.*, [2] 83, 271 (1861).

[3] *Loc. cit.*

g. hydrazine hydrate 16–18 g. of hydrazinodiacetic acid, which he reports as a 51–57% yield, but it should be observed that this calculation is based on the amount of monochloroacetic acid used (40 g.). Calculated the other way, the yield dwindles to 10 8-12.2%. We obtained from 21 g. of hydrazine hydrate 21.5 g. of recrystallized hydrazinodiacetic acid, which represents a yield of 34.6%, calculated on the basis of the hydrazine hydrate used.

Two methods were investigated for isolating semicarbazinodiacetic acid from the salt mixture formed in its preparation. The method that gave the best yield was esterification with alcoholic hydrochloric acid. As semicarbazinodiacetic acid forms a very difficultly soluble barium salt, an attempt was made to utilize this salt in the isolation of the semicarbazinodiacetic acid, but the method was not perfected to the point where the yield was equal to that in the esterification process.

The esters of semicarbazinodiacetic acid are readily oxidized with permanganate or bromine. The oxidation results in the elimination of one acetic acid rest, with the formation of esters of the semicarbazone of glyoxylic acid, $NH_2CONHN = CHCOOH$. The ethyl ester of this semicarbazone was first prepared by Simon and Chavenne.[1] Their description of the substance does not agree with the properties of the semicarbazone as determined by us. However, the constitution of the oxidation product of ethyl semicarbazinodiacetate was established beyond question by its formation, (a) on esterification of glyoxylic acid semicarbazone, and (b) on oxidation of ethyl semicarbazinomonoacetate. Furthermore, on reduction with sodium amalgam, according to the method of Darapsky and Prabhaker,[2] the oxidation product of ethyl semicarbazinodiacetate gave semicarbazinoacetic acid, $NH_2CONHNHCH_2COOH$, which was isolated by esterification. The ethyl ester obtained in this way proved identical in its properties with the semicarbazinoacetic ester prepared by Traube from the hydrochloride of ethyl hydrazinoacetate and potassium cyanate.[3]

With sodium alcoholate, the esters of semicarbazinodiacetic acid, analogous to esters of semicarbazino acids in general,[4] condense to esters of 3,5-dioxy-1,6-dihydro-1,2,4-triazine-1-acetic acid,

$$\begin{array}{c} N\text{---}CH_2COOH \\ \diagup \diagdown \\ CH_2 \quad N \\ | \qquad \| \\ HO\text{---}C \quad C\text{---}OH \\ \diagdown \diagup \\ N \end{array}$$
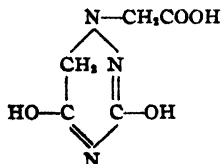
[1] Compt. rend., 143, 1906 (1906).
[2] Ber., 45, 2625 (1912).
[3] Ibid., 31, 164 (1898).
[4] Am. Chem. J., 28, 386 (1902)

Boiled with the calculated amount of alkali, the esters of semicarbazino-diacetic acid are readily saponified to semicarbazinodiacetic acid; but, if heated under pressure at 150° with potassium hydroxide, semicarbazino-diacetic acid readily loses the carbonamide rest with the formation of hydrazinodiacetic acid,

$$NH_2CONHN(CH_2COOH)_2 + 3KOH =$$
$$NH_2N(CH_2COOK)_2 + KHCO_3 + H_2O.$$
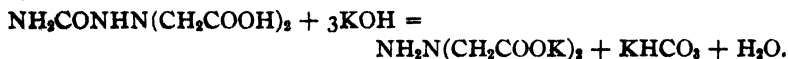
The constitution of hydrazinodiacetic acid and semicarbazinodiacetic acid was established conclusively by the action of sodium nitrite on hydra-zinodiacetic acid and on methyl semicarbazinodiacetate, in which reactions iminoacetic acid, $NH(CH_2COOH)_2$, and methyliminodiacetate, respectively, are readily formed and proved identical with the same preparations as described by other investigators. Curtius and Hussong · tried the action of nitrous acid on hydrazinodiacetic acid, but did not succeed in isolating iminodiacetic acid. The behavior of hydrazino- and semicarbazino-diacetic acids towards nitrous acid is analogous to that of asymmetric methylphenylhydrazine, $NH_2N(CH_3)C_6H_5$,[1] and diethyl-semicarbazide, $NH_2CONHN(C_2H_5)_2$,[2] towards nitrous acid. The following equations interpret the reactions that take place between nitrous acid and the above hydrazine derivatives of acetic acid:

$$NH_2N(CH_2COOH)_2 + HNO_2 = NH(CH_2COOH)_2 + H_2O + N_2O$$
$$NH_2CONHN(CH_2COOCH_3)_2 + HNO_2 =$$
$$NH(CH_2COOCH_3)_2 + N_2O + CO_2 + NH_3$$
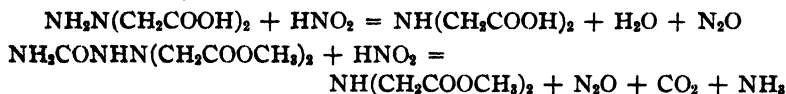
Curtius and Hussong found that hydrazinodiacetic acid very readily decomposes on heating with mineral acids, in that half of the nitrogen in the molecule is eliminated as ammonia. In addition to confirming this observation, we were able to isolate among the reaction products glyco-coll and nitrilotriacetic acid, $N(CH_2COOH)_3$. The primary organic complex of the hydrolysis of the hydrazine acid is assumed by Curtius and Hussong to be hydroxylaminodiacetic acid. The formation of glycocoll from hydroxylaminodiacetic acid may be explained by assuming the elimination of a molecule of water and the subsequent hydrolysis of the resulting products as follows:

$$HON(CH_2COOH)_2 = (CH_2COOH)N = CHCOOH + H_2O.$$
$$(CH_2COOH)N = CHCOOH + H_2O = NH_2CH_2COOH + CHOCOOH.[3]$$
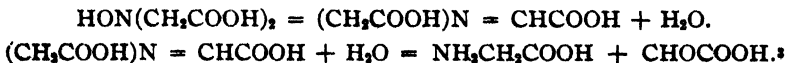
It may be that a second form of hydrolysis proceeds along with the one suggested above in that a part of the hydrazinoacetic acid breaks down into glycollic acid and hydrazinomonoacetic acid as primary decomposition products,

[1] *Ann.*, **190**, 158 (1878).

[2] *Ibid.*, **199**, 314 (1879).

[3] Cf. *Ber.*, **39**, 2566 (1906).

$$NH_2N(CH_2COOH)_2 + H_2O = NH_2NHCH_2COOH + CH_2OHCOOH.$$

The interaction of glycollic acid and glycocoll could then explain the formation of nitrilotriacetic acid,

$$2CH_2OHCOOH + NH_2CH_2COOH = N(CH_2COOH)_3 + 2H_2O.$$

The assumption that glycollic acid is an intermediary product in the action of sulfuric acid on hydrazinodiacetic acid harmonizes with the behavior of semicarbazinodiacetic acid esters toward oxidizing agents, which, as shown above, results in the elimination of an acetic acid rest without a severance of the two nitrogen atoms in the original hydrazine complex.

The formation of nitrilotriacetic acid in the interaction of sulfuric acid and hydrazinodiacetic acid was quite unexpected, because Heintz found that nitrilotriacetic acid, heated with concentrated hydrochloric acid for 17 hrs. at 190° to 200°, was converted to iminodiacetic acid.[1]

However, a repetition of our experiment with hydrazinodiacetic acid gave the same uniform result. Attention might be called to the fact that this elimination of an acetic acid rest from nitrilotriacetic acid by hydrolysis, as observed by Heintz, is also strictly analogous to the second form of hydrolysis suggested above for hydrazinodiacetic acid.

In confirming the constitution of the oxidation product of ethyl semicarbazinodiacetate, as described above, the semicarbazone was reduced with sodium amalgam, according to the method of Darapsky and Prabhaker, and in this way semicarbazinoacetic acid resulted. These investigators do not isolate in their process the semicarbazino acid as such, but convert it to the hydrazino acid by the action of concentrated hydrochloric acid, and isolate the hydrazine in the form of the hydrochloride of the ethyl ester, $HCl.NH_2NHCH_2COOC_2H_5$. We discovered that semicarbazinoacetic acid itself is readily esterified and likewise forms a hydrochloride difficultly soluble in alcohol, so that an excellent method of preparing semicarbazino acids is suggested.

As shown in the experimental part of this article, this method may be used to prepare semicarbazinopropionic acid, $NH_2CONHNHCH(CH_3)COOH$, from the semicarbazone of pyruvic acid,

$$NH_2CONHN = CH(CH_3)COOH.$$

Besides Darapsky and Prabhaker, Emil Fischer,[2] Elbers,[3] and later Kessler and Rupe,[4] have effected the reduction of the N = C complex in hydrazones with sodium amalgam.

The ethyl ester of semicarbazinoacetic acid reacts with mustard oils to form thiohydantoins.[5] With benzoyl chloride, the ester gives a benzoyl

[1] *Ann.*, 149, 88 (1869).
[2] *Ber.*, 16, 2241 (1883).
[3] *Ann.*, 227, 354 (1885).
[4] *Ber.*, 45, 26 (1912).
[5] *This Journal*, 26, 1006 (1904).

derivative, which, with alkali, loses a molecule of water with the formation of a triazol.[1] The semicarbazino ester further condenses with sodium alcoholate to the sodium salt of 3,5-dioxy-1,6-dihydro-1,2,4-triazine.[2] The hydrochloride of the ester yields, with sodium nitrite, a beautifully crystallizing nitroso derivative.

The isolation of nitroso-derivatives of semicarbazino acids extends the analogy between the semicarbazino acids and secondary amines, which show a like behavior toward acid chlorides, mustard oils, isocyanates, nitrous acid, and diazonium salts,[3] as has been demonstrated by investigations carried out in this laboratory. It is the α-nitrogen in the semicarbazino acids to which is joined the reactive hydrogen, just as in the case of phenyl semicarbazide.

Experimental Part.

Preparation of Methyl and Ethyl Esters of Semicarbazinodiacetic Acid.—
A semicarbazide solution is prepared according to the method of Bouveault and Locquin[4] in the following way: "130 g. (1 mol) hydrazine sulfate are dissolved in 500 cc. of boiling water, and to the hot solution 69 g. (0.5 mol) of potassium carbonate added in small portions. After allowing the solution to cool, 81 g. of potassium cyanate (1 mol) are added in several portions with the precaution of not allowing the temperature to rise. After this solution has stood 12 to 15 hrs., the potassium sulfate is precipitated in great part by the addition of 300 cc. of absolute alcohol and filtered off." This solution is assumed to contain 80% of the theoretical yield of semicarbazide. A concentrated aqueous solution of 227 g. of monochloroacetic acid (3 mols) is next prepared and neutralized with 165.5 g. of potassium carbonate (1.5 mols). The semicarbazide solution is now mixed with the potassium chloroacetate solution, and, after the reaction has proceeded in a boiling water bath for 12 hrs., the solution is evaporated to dryness *in vacuo.* For esterification, it is best to crush the flask and cut the sticky salt cake into small bits. Prepared in this way, the salt cake, on boiling with alcohol, disintegrates into a form suitable for the action of alcoholic HCl, and after this preliminary treatment, is allowed to stand with 300 cc. of 8% alcoholic acid for one week. At the end of this time, to the alcoholic solution of the ester filtered from inorganic salts, there is added a slight excess of ammonia, the alcohol is then distilled off *in vacuo,* the residue taken up in water, and the ester extracted with chloroform. A small amount of ester may be obtained by re-esterification of the salt residue obtained from the mother liquor left after extracting the ester as above with chloroform. 130 g. of hydrazine sulfate

[1] Cf. *Ber.,* **33,** 1520 (1912)
[2] *Loc. cit.*
[3] THIS JOURNAL, **29,** 881 (1907).
[4] *Bull. soc. chim.,* **33,** 162 (1903).

worked up in the above way gave 34.9 g. of the methyl ester, and a second experiment to determine the yield of ethyl ester resulted in 39.3 g. of the latter substance. Figured on the basis of the hydrazine sulfate employed, the yield in either case is approximately 16%.

Methyl Semicarbazinodiacetate, $NH_2CONHN(CH_2COOCH_3)_2$.—This ester can be purified by crystallization from alcohol or water. From alcohol it separates in long needles, which melt undecomposed at 143.5°. It is readily soluble in chloroform and water, more difficultly soluble in benzene, and only slightly soluble in ether

Calc. for $C_7H_{13}O_5N_3$: C, 38.36; H, 5.93; N, 19.18. Found· C, 38.10; H, 6.06; N, 18.97.

Ethyl Semicarbazinodiacetate, $NH_2CONHN(CH_2COOC_2H_5)_2$.—The ethyl ester is more readily soluble than the methyl ester in all solvents. It is best purified by crystallization from ether, from which it separates slowly in a fine, granular, crystalline state. From benzene it is obtained in the form of thin plates with dome shaped end faces, as seen under the microscope, and melts to a clear liquid at 91°.

Calc. for $C_9H_{17}O_5N_3$: C, 43.72; H, 6.88; N, 17.00. Found: C, 43.52, 43.70; H, 7.05, 6.93; N, 16.79, 17.15.

Semicarbazinodiacetohydrazide, $NH_2CONHN(CH_2CONHNH_2)_2$.—Hydrazine hydrate (2 mols) and methyl semicarbazinodiacetate (1 mol) mixed in concentrated aqueous solution react readily at water bath temperature. The hydrazide, which separates out, can be purified by precipitation from a concentrated solution in water with alcohol. It melts at 149°, decomposing on heating a few degrees higher.

Calc. for $C_5H_{13}O_3N_7$: C, 27.40; H, 5.94; N, 44.75. Found: C, 27.23; H, 6.05; N, 44.85.

Dibenzal-semicarbazinodiacetohydrazide, $NH_2CONHN(CH_2CONHN = CHC_6H_5)_2$.—On agitating an aqueous solution of the hydrazide with benzaldehyde, the benzal compound quickly precipitates in quantitative yield. Purified by crystallization form alcohol, it melted at 178° with gas evolution.

Calc. for $C_{19}H_{21}O_3N_7$: N, 24.81. Found: N, 24.85.

Action of Nitrous Acid on Methyl Semicarbazinodiacetate.- · When equimolecular amounts of methyl semicarbazinodiacetate, sodium nitrite, and hydrochloric acid are brought together in water as a solvent, the solution immediately assumes a deep yellow color and simultaneously a slow, steady gas evolution begins. The gas has the characteristic odor of nitrous oxide, and is mixed with carbon dioxide. After several hours' standing, the gas evolution stops and the original yellow color of the solution is almost completely discharged. The methyliminodiacetate formed can be removed by extraction with ether, from which it precipitates as a hydrochloride, on leading into the ether hydrochloric acid

gas. This substance is described by Jongkees.[1] He gives the decomposition point as 183°, which agrees with our observation, when the substance is rapidly heated.

Calc. for $C_4H_{11}O_4N.HCl$: N, 7.09; HCl, 18.48.   Found: N, 7.38; HCl, 18.73.

Esters of 3,5-Dioxy-1,6-dihydro-1,2,4-triazine-1-acetic Acid,
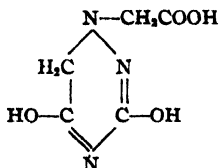
Ethyl Ester.—When treated with one mol of sodium ethoxide in ethyl alcohol solution, ethyl semicarbazinodiacetate loses a molecule of alcohol passing to the sodium salt of the ester of the above triazine acid. The same substance is obtained when methyl semicarbazinodiacetate is treated with sodium ethoxide in ethyl alcohol solution. If, on the other hand, the ethyl ester of the semicarbazino acid is treated with sodium methoxide in methyl alcohol solution, a salt of the methyl ester of the triazin acid results. In the preparation of the ethyl ester, a solution of sodium ethoxide, from o.7 g. metallic sodium and 5 cc. of ethyl alcohol, was added to 5 g. of methyl semicarbazinodiacetate in 25 cc. of ethyl alcohol. A sodium salt of the triazine ester separated out, but this was not filtered off. After 5 hrs. 35 cc. N HCl was added, the slight excess of HCl neutralized with ammonia, the solution evaporated to dryness, the residue taken up with a little water, and the triazine extracted with chloroform. This product proved identical with the triazine prepared by substituting the ethyl ester of semicarbazinodiacetic acid for the methyl ester in the above experiment. The new substance can be crystallized from water, alcohol, or acetic ether, in all of which solvents it is readily soluble. It is more difficultly soluble in benzene, and very sparingly soluble in ether. From alcohol it crystallizes in radiating bunches of short slender needles, which melt undecomposed at 138.5°.

Calc. for $C_7H_{11}O_4N_3$: C, 41.79; H, 5.47; N, 20.90.   Found: C, 41.59, 41.55; H, 5.43, 5.57; N, 20.84.

Methyl Ester.—The triazine methyl ester was prepared similarly to the ethyl ester from both methyl and ethyl semicarbazinodiacetate. The yield of ester obtained here was about 70% of the theoretical. This ester is much more difficultly soluble in water than is the corresponding ethyl ester, so that it separates out in great part, when, in its preparation, the sodium salt of the triazine ester is neutralized with HCl. The methyl ester is readily soluble in hot water, less soluble in alcohol, difficultly

1 *Rec. trav. chim.*, 27, 287 (1908).

soluble in chloroform and acetic ether, and insoluble in ether. From water, the methyl ester crystallizes in characteristic short, thick prisms with dome shaped end faces, melting undecomposed at 183.5°.

Calc. for $C_5H_9O_4N_3$: C, 38.50; H, 4.81; N, 22.46.   Found: C, 38 33; H, 4.93; N, 22.77.

Semicarbazinodiacetic Acid, $NH_2CONHN(CH_2COOH)_2$.—The esters of semicarbazinodiacetic acid are readily saponified by boiling with the calculated amount of potassium hydroxide solution. For the isolation of the semicarbazinodiacetic acid, the potassium salt, as thus prepared, is treated with the requisite quantity of hydrochloric acid, the solution evaporated to dryness, and the residue extracted with alcohol. The acid precipitates from the alcohol in a fine granular condition on the addition of ether. It can also be obtained as a barium salt directly from the reaction product of potassium monochloroacetate on semicarbazide by neutralizing the reaction mixture with barium hydroxide, whereupon the difficultly soluble barium salt separates out. From this salt, the semicarbazino acid can be obtained in the usual way by removing the barium as sulfate. The acid may be recrystallized from either alcohol or water in long rectangular plates, which on heating decompose with gas evolution at 161°. It has a very acid taste. The barium, calcium and z·nc salts are difficultly soluble in water. Treated with sodium nitrite, an aqueous solution of the acid assumes a deep yellow color, but the nitroso compound here formed immediately begins to decompose with gas evolution. The acid titrates dibasic.

Calc. for $C_5H_9O_5N_3$: C, 31.41; H, 4.71; N, 21.99.   Found: C, 31.15; H, 4.77; N, 22.25

Calcium Semicarbazinodiacetate, $C_5H_7O_5N_3Ca.4.5H_2O$.—For the prepara·tion of the salts of semicarbazinodiacetic acid, a solution of the potassium salt was made, which with soluble salts of calcium, barium and zinc shows a precipitation. These salts are all difficultly soluble in water, and were not recrystallized for analysis. The calcium salt separates slowly from solution in the form of short, thick prisms. For the complete dehydration of the salt, we employed a temperature of 180°.

Calc. for $C_5H_7O_5N_3Ca.4H_2O$: Ca, 12.90; H_2O, 26.13.   Found: Ca, 12.70, 12.69; H_2O, 26.54.

Barium Semicarbazinodiacetate, $C_5H_7O_5N_3Ba.H_2O$.—The barium salt, prepared by adding barium chloride to a solution of potassium semicarbazinodiacetate, shows no definite crystalline form under the microscope. Our analysis indicates the presence of a molecule of water of crystallization, but the salt showed no loss in weight on heating as high as 180°.

Calc. for $C_5H_7O_5N_3Ba.H_2O$: Ba, 39.89; N, 12.21.   Found: Ba, 39.52, 39.82; N, 12.35.

Zinc Semicarbazinodiacetate, $C_5H_7O_5N_3Zn.H_2O$.—The zinc salt, made by the method employed for the calcium and barium salts, was obtained

in the form of thin plates with dome-shaped end faces, as seen under the microscope. The zinc determination on a sample of the salt dried at 100° indicates a molecule of water of crystallization.

Calc. for $C_8H_7O_4N_2Zn.H_2O$: Zn, 24.01.   Found: Zn, 24.15.

Preparation of Hydrazinodiacetic Acid, $NH_2N(CH_2COOH)_2$, *from Methyl Semicarbazinodiacetate*.—As hydrazinodiacetic acid is decomposed by acids similar to nitrilotriacetic acid, it was attempted to split off the urea rest from the semicarbazino ester with alkali. In this experiment the conditions followed were to heat the semicarbazino ester with 3 mols of $3N$ KOH in a sealed tube at 150° for two hrs. At the end of this time the ammonia was distilled off and 3 mols of standardized HCl added. On concentration of the solution to a point just sufficient to hold the inorganic salts in solution, the hydrazinodiacetic acid crystallized out in a yield of about 75% to 80% of the theoretical. In one experiment the yield of hydrazinodiacetic acid obtained was 77% of the theoretical, and a titration of the ammonia liberated in the reaction indicated a decomposition of 75.76%. There is necessarily a slight loss of ammonia in the transfer from the pressure tube to the distilling flask, and a further slight discrepancy in the results may be accounted for by a small amount of potassium chloride in the hydrazine acid as weighed. On evaporation of the filtrate from the hydrazine acid and esterification of the residue with 8% ethyl alcoholic HCl in the cold, about 15% of the original semicarbazino ester may be regained.

Hydrazinodiacetic acid can also be prepared by the action of KOH at 150° on the barium salt of semicarbazinodiacetic acid, as obtained above directly from the reaction product of potassium chloroacetate on semicarbazide, but the yield obtained by this method was not satisfactory.

Preparation of Hydrazinodiacetic Acid from Potassium Chloroacetate and Hydrazine Hydrate.[1]—The following modification of the method of Curtius and Hussong is to be recommended in the preparation of hydrazinodiacetic acid. Neutralize 80 g. of monochloroacetic acid (2 mols) in 200 cc. of water by adding in small portions 58 g. of potassium carbonate (1 mol) and then pour into this solution of potassium chloroacetate 21 g. of hydrazine hydrate (1 mol). A second 58 g. of potassium carbonate are now added gradually, whereupon, with a steady evolution of CO_2, the temperature rises to about 70°. The solution is now heated as long as gas evolution continues. At the end of the reaction, the hydrazinodiacetic acid is precipitated by making the solution acid to Congo paper with hydrochloric acid.[2]

[1] *J. prakt. Chem.*, [2] 83, 271 (1861).

[2] The following conditions were established as suitable for the preparation of hydrazinomonoacetic acid from potassium chloroacetate and hydrazine hydrate: Into 42 g. of 50% hydrazine hydrate (Kahlbaum), allow to drop rapidly with constant stirring, a solution of potassium chloroacetate, prepared from 21 g. of potassium car-

The hydrazine acid thus obtained is freed from any admixed potassium chloride by recrystallization from water. The hydrazinodiacetic acid, obtained by the action of potassium hydroxide on the methyl ester of semicarbazinodiacetic acid, proved identical with the above preparation from hydrazine hydrate. Curtius and Hussong state that the hydrazine acid, on heating, melts with violent gas evolution at 166°–167°. Our observation is that the substance begins to take on a yellow color at 165° and decomposes suddenly and completely at 176°. Despite the fact that the substance contains two carboxyls it has not an acid taste. Its solubility in water is 1:108 at 22° and 1:46 at 100°. The following analysis was made on a sample obtained from the ester of semicarbazino-diacetic acid.

Calc. for $C_4H_8O_4N_2$: C, 32.43, H, 5.41; N, 18.92. Found: C, 32.26; H, 5.53; N, 18.86.

Barium Hydrazinodiacetate, $C_4H_6O_4N_2Ba.H_2O$.—The barium salt of hydrazinodiacetic acid was made by adding the calculated amount of barium chloride to a solution of the acid, neutralized with potassium hydroxide. The barium salt separates out slowly in a finely divided state, showing no definite crystalline form. Heated to 150°, it loses one molecule of water.

Calc. for $C_4H_6O_4N_2Ba.H_2O$: Ba, 45.58; H_2O, 5.98. Found: Ba, 44.74; H_2O, 6.53.

Zinc Hydrazinodiacetate, $C_4H_6O_4N_2Zn$.—The zinc salt was prepared similarly to the barium salt and resembles it very closely in its physical properties. Neither the barium nor zinc salt could be purified by recrystallization.

Calc. for $C_4H_6O_4N_2Zn$: Zn, 31.03. Found: Zn, 30.81.

Esters of Hydrazinodiacetic Acid.—Curtius and Hussong prepared the ethyl ester of hydrazinodiacetic acid from the silver salt of the acid and bonate and 29 g. of monochloroacetic acid (1 mol.). At the same time add, in small quantities, a second batch of 21 g. of potassium carbonate to the hydrazine solution, timing the process so as to bring it to a close with the addition of the potassium chloro-acetate. To insure completion of the reaction, next heat the solution to boiling one-half hour. In this reaction there is formed both the hydrazinomono- and di-acetic acid The latter separates on making the solution acid with hydrochloric acid For the isolation of the hydrazinomonoacetic acid, the solution, filtered from the hydrazinodi-acetic acid, is evaporated to dryness, 150 cc. of alcohol poured on the salt cake, and finally hydrochloric acid gas led in to saturation. The esterification is then allowed to proceed in the cold twelve hours, when the solution is heated to boiling and filtered hot from the salt residue. On cooling, the hydrochloride of the hydrazino ester crystallizes out. The yields, in the one experiment tried, were 16 g. of hydrazinodiacetic acid and 7.3 g. of the hydrochloride of hydrazinomonoacetic acid ethyl ester. Darapsky and Prabhaker[4] obtained from 20 g. of hydrazine hydrate (equal to 40 g. of 50% hydrate used above) 6.4 g. of the hydrochloride of the ester of hydrazinoacetic acid, using a method similar to that of Curtius and Hussong for preparing hydrazinodiacetic acid.—J. R. BAILEY and L. A. MIKESKA, *Ber.*, 45, 1660 (1912).

ethyl iodide, and found it to be a "syrup," which they were unable to crystallize. The same substance was obtained by esterification with alcoholic HCl. We repeated their last experiment and obtained the hydrochloride of the ethyl ester as a viscous oil, readily soluble in alcohol, but which we were unable to crystallize. On dissolving in a concentrated aqueous solution of this salt an equimolecular amount of potassium cyanate, ethyl semicarbazinodiacetate crystallized out after stirring a few minutes, and proved identical with the esterification product of the acid already described, obtained by the interaction of potassium chloroacetate and semicarbazide. A nitrogen determination was made on the semicarbazino ester made by this second process.

Calc. for $C_9H_{17}O_5N_3$: N, 17.00. Found: N, 17.30.

Hydrazinodiacetic acid is insoluble in both ethyl and methyl alcohol, but quickly dissolves in either with rapid esterification on leading hydrochloric acid gas into a suspension of the acid in alcohol. We found that the methyl ester gives a beautifully crystallizing hydrochloride. For analysis it was crystallized from methyl alcohol in slender microscopic needles, which melted with gas evolution at 174.5°.

Calc. for $C_6H_{12}O_4N_2$.HCl: N, 13.13; HCl, 17 18. Found: N, 13.33; HCl, 17.10.

This salt was likewise converted to the semicarbazino ester by the action of potassium cyanate, and the substance thus obtained proved identical with the esterification product of CH_3OH-HCl on semicarbazinodiacetic acid. As a further confirmation, a nitrogen determination was made.

Calc. for $C_7H_{13}O_5N_3$: N, 91.18. Found: N, 19.41.

Phenylthioureidaminodiacetic Acid Methyl Ester, $C_6H_5NHCSNHN-(CH_2COOCH_3)_2$.—The above substance was prepared by dissolving the hydrochloride of hydrazinodiacetic acid methyl ester and sodium bicarbonate in equimolecular amounts in a little water, adding one mol of phenyl mustard oil dissolved in alcohol, and heating this mixture one hour to boiling. The alcohol was then distilled off and the mustard oil compound crystallized from alcohol, from which it separated in long needles, melting undecomposed at 120°. This compound is readily soluble in the common solvents with the exception of ether, petrolic ether, and water.

Calc. for $C_{13}H_{17}O_4N_3S$: N, 13.55. Found: N, 13.56.

Action of Formaldehyde on Hydrazinodiacetic Acid.—All attempts of Curtius and Hussong to condense hydrazinodiacetic acid with aldehydes were without results. We repeated some of their experiments in this direction and were likewise unable to bring about a reaction. However, formaldehyde reacts in a peculiar way with this hydrazine. If hydrazinodiacetic acid be covered with ordinary formalin, the hydrazine after a short time dissolves, forming a yellow solution, which becomes red on standing. If the hydrazine be warmed with the formaldehyde solution,

it immediately dissolves with a violent evolution of carbon dioxide, and the reaction product can be precipitated by the addition of alcohol as a crystalline, slightly yellow substance, which was not further investigated.

Conversion of Hydrazinodiacetic Acid to Iminodiacetic Acid by the Action of Sodium Nitrite.—To 2 g. of the hydrazine acid covered with 15 cc. of water were added 1 g. of sodium nitrite and 5 cc. of water. The hydrazine dissolved after a few minutes stirring, with an evolution of a colorless gas, probably N_2O. At the end of the reaction, the calculated amount of standard hydrochloric acid was added to liberate the iminodiacetic acid, and the solution was then concentrated to a small volume. After standing over night, 1.2 g. of the characteristic crystals of iminodiacetic acid separated out. This product proved identical with a sample made according to the method of Heintz.[1] Eschweiler found that this substance melts with decomposition at about 225°,[2] while Johnson gives the decomposition point at 235-236°.[3] Our determination agreed with that of Johnson.

Calc. for $C_4H_7O_4N$: C, 36.09; H, 5.26; N, 10.53. Found: C, 36.06; H, 5.36; N, 10.66.

Action of Sulfuric Acid on Hydrazinodiacetic Acid.—In one experiment 0.5 g. of hydrazinodiacetic acid was heated in a sealed tube with 10 cc. of 2.85 N H_2SO_4 2 hrs. at 150°. The solution was then made alkaline with a slight excess of barium hydroxide and the liberated ammonia estimated. Calculated for 1 mol of ammonia, 3.38 cc. N acid; used, 3.65 cc. This result agrees with a similar determination made by Curtius and Hussong in their study of the action of acids on hydrazinodiacetic acid. After exact removal of the barium as sulfate, the solution from the ammonia distillation was evaporated to dryness and the residue purified to some extent by dissolving in water and precipitating with alcohol. A substance was thus obtained which, on heating, began to show signs of decomposition at about 200°, contracted on further heating, and decomposed completely between 225° and 230° (uncor.). This observation agrees quite well with the behavior of glycocoll on heating. In order to confirm fully the formation of glycocoll in the above decomposition of hydrazinodiacetic acid, the experiment was repeated though with slight modification. In this second experiment 5 g. of hydrazinodiacetic acid and 20 cc. of 7.7 normal sulfuric acid were heated two hours at 150°. There was considerable pressure on opening the tube, and after standing three days, 0.5 g. of a crystalline substance had separated out. This proved to be Heintz's "Triglycolamidsäure," $N(CH_2COOH)_3$.[4] It was compared with a sample of nitrilotriacetic acid, made according to

[1] *Ann.*, **122**, 257 (1862).
[2] *Ibid.*, **278**, 231 (1894).
[3] *Am. Chem. J.*, **35**, 65 (1907).
[4] *Ann.*, **122**, 269 (1862).

the method of Heintz, and in addition a nitrogen determination was made. According to our observation, nitrilotriacetic acid decomposes at 246° to a reddish brown liquid. Polstorff and Meyer[1] give 239° as the decomposition point (probably uncor.).

Calc. for $C_6H_9O_6N$: N, 7.33.   Found: N, 7.69.

The acid filtrate from the nitrilotriacetic acid was heated with an excess of barium carbonate, and after removal of the barium salts the dissolved barium was precipitated as sulfate. The residue obtained by evaporating the filtered solution was taken up with water, and after neutralization with the calculated amount of potassium hydroxide, shaken with a slight excess of phenylisocyanate, according to the method of Paal.[2] A small amount of diphenyl urea was filtered off, and the solution made acid with hydrochloric acid. 1.5 g. of phenylureidoacetic acid crystallized out. This was compared with a preparation made according to the method of Paal. On heating with concentrated hydrochloric acid, this hydantoic acid showed the behavior of phenylhydantoic acid, as recorded by Mouneyrat,[3] in that it was converted to 2-phenylhydantoin, melting at 159 to 160°. A nitrogen determination, made on the phenylureidoacetic acid, gave the following result:

Calc. for $C_9H_{10}O_3N_2$: N, 14.43.   Found: N, 14.75.

Oxidation of the Esters of Semicarbazinodiacetic Acid. Ethyl Ester of Glyoxylic Acid Semicarbazone, $NH_2CONHN = CHCOOC_2H_5$.—When to a concentrated aqueous solution of the ethyl ester of semicarbazinodiacetic acid, made acid with sulfuric acid, a concentrated solution of potassium permanganate is added, oxidation proceeds for some time without gas evolution, and after a while a difficultly soluble substance separates, which proved to be the semicarbazone of glyoxylic acid ethyl ester. The yield is poor and we did not attempt to isolate any other products of the reaction. It is possible that ethyl glycolate is formed as an intermediary product, but according to Schreiner[4] this ester would immediately be saponified by water into the corresponding acid. Although the oxidation proceeds for some time without gas evolution, the primary oxidation products later decompose on further addition of permanganate with gas evolution. The ethyl ester of glyoxylic acid semicarbazone was also pre-prepared by oxidizing with permanganate Traube's ethyl semicarbazino-acetate,[5] the reaction proceeding here similarly to the oxidation of ethyl semicarbazinopropionate.[6] The structure of the ester of glyoxylic acid

[1] *Ber.*, **45**, 1910 (1912).

[2] *Ibid.*, **27**, 975 (1894).

[3] *Ibid.*, **33**, 2394 (1900).

[4] *Ann.*, **197**, 7 (1879).

[5] *Ber.*, **31**, 166 (1898).

[6] *Ann.*, **303**, 83 (1898).

semicarbazone was further confirmed by esterifying with alcoholic hydrochloric acid glyoxylic acid semicarbazone, which had been prepared from chloral hydrate and semicarbazide. A substance of the formula $NH_2CONHN = CHCOOC_2H_5$ is described by Simon and Chavanne,[1] but the properties of their semicarbazone do not agree with those, as determined by us, for the oxidation product of ethyl semicarbazinodiacetate. They describe their product as follows: "It melts with decomposition at 228°, is apparently insoluble in almost all solvents, but is readily soluble in boiling water with partial saponification." We find that the substance, when slowly heated, melts with gas evolution to a brown liquid at 211°, but on rapid heating, the decomposition takes place at about 218°. Our preparation was purified by crystallization from water and alcohol. In recrystallizing from water, it did not show any tendency to saponify. The substance crystallized from alcohol has the form of long, slender prisms, the faces of which have the appearance of being etched.

Calc. for $C_5H_9O_4N_3$: C, 37.71; H, 5.63; N, 26.42. Found: C, 37.57; H, 5.63; N, 26.60

The above ester was prepared as follows from glyoxylic acid semicarbazone, obtained by the action of chloral hydrate on semicarbazide:[2] 3 g. of the semicarbazone acid were suspended in 150 cc. of 8% alcoholic hydrochloric acid and the solution heated to boiling 45 min. The alcohol was then distilled off, the residue taken up with a little water and made slightly alkaline with ammonia. The semicarbazone ester prepared in this way has a slight yellow color, which is completely removed by recrystallization from water with the addition of animal charcoal.

Oxidation of Methyl Semicarbazinodiacetate with Bromine.—Only a very small yield of the semicarbazone methyl ester was obtained by oxidizing the semicarbazino methyl ester with potassium permanganate. The esterification was therefore carried out with bromine under the following conditions: 5 g. of the semicarbazino methyl ester were dissolved in 40 cc. of water and 1.5 cc. of bromine (1.2 cc. corresponds to one mol) aspirated into this solution. The bromine was instantaneously reduced and 0.75 g. of the oxidation product separated out, corresponding to 22.7% of the theoretical yield of semicarbazone. This semicarbazone is readily soluble in hot water, and more difficultly soluble in alcohol. It crystallizes from water in a fine, granular condition. If it is heated and the bath kept at 206° for a few minutes it melts completely at this temperature with decomposition.

Calc. for $C_4H_7O_3N_3$: C, 33.10; H, 4.83; N, 28.97. Found: C, 33.27; H, 4.97; N, 29.31.

[1] *Compt. rend.,* 143, 904 (1906).
[2] *Ber.,* 45, 2624 (1912).

Preparation of Ethyl Semicarbazinoacetate, $NH_2CONHNHCH_2COOC_2H_5$, *from Semicarbazide and Monochloroacetic Acid.*—In the action of potassium chloroacetate on semicarbazide, there is always formed both semicarbazinomono- and di-acetic acid. In the preparation of the former substance, it is best to use only one-third of the potassium chloroacetate recommended above in the preparation of the diacetic derivative. Esterification of the semicarbazinoacetic acid is best effected with boiling 3% alcoholic HCl, from which the HCl salt of the ester crystallizes on cooling. The yield of semicarbazinoacetic acid ethyl ester, obtained by this method, was only 3 g. from 40 g. of semicarbazide. Purified by recrystallization from alcohol, the ester melted at 122°, as reported by Traube,[1] and proved identical with the ester obtained below by reducing glyoxylic acid semicarbazone and esterifying the reduction product.

Calc. for $C_5H_{11}O_3N_3$: C, 37.27; H, 6.83; N, 26.08. Found: C, 37.32; H, 6.96; N, 26.33.

Preparation of Ethyl Semicarbazinoacetate by Esterification of the Reduction Product of Glyoxylic Acid Semicarbazone.—11.8 g. of glyoxylic acid semicarbazone were reduced with sodium amalgam, according to the directions of Darapsky and Prabhaker,[1] after neutralization of the reduction liquid with hydrochloric acid, the solution was evaporated to dryness, and the residue esterified by boiling with 250 cc. of 3% alcoholic hydrochloric acid for one hour. The alcohol solution was filtered hot from the insoluble inorganic salts. On cooling, 9.2 g. of the hydrochloride of the ethyl ester of semicarbazinoacetic acid crystallized out. The filtrate from the hydrochloride of the ester was put back on the salt mass and boiled another hour. The alcohol was then filtered off, the HCl neutralized with ammonia, the boiling solution filtered from the ammonium chloride, and the filtrate evaporated to dryness. The residue, on extraction with alcohol, yielded 4 g. of crude semicarbazino ester, which gave 2.1 g. pure substance on recrystallization. The total yield was about 66% of the theoretical. Darapsky and Prabhaker obtained a yield of 50.4% of the theoretical in working up the reduction product of glyoxylic acid semicarbazone to the HCl salt of the ethyl ester of hydrazinoacetic acid, $HCl.NH_2NHCH_2COOC_2H_5$. For analysis the hydrochloride of semicarbazinoacetic acid ethyl ester was recrystallized from alcohol. It decomposes at 178° with gas evolution.

Calc. for $C_5H_{11}O_3N_3.HCl$: N, 21.27; HCl, 18.50. Found: N, 21.42; HCl, 18.53.

Semicarbazinoacetic Acid, $NH_2CONHNHCH_2COOH$.—The ester of semicarbazinoacetic acid is readily saponified by digestion for one-half hour in aqueous solution with one-half mol of barium hydroxide. On allowing the reaction mixture to cool, the difficultly soluble barium salt crystallizes out, from which the acid can be liberated by exactly removing

[1] *Loc. cit.*

the barium as sulfate and concentrating the solution to the point of crystallization.   It is readily soluble in water and difficultly soluble in alcohol   The acid melts at 143°

Calc for $C_6H_7O_3N_3$ N, 31 58   Found N, 31 86

Benzoyl Derivative of Ethyl Semicarbazinoacetate, $NH_2CONHN(COC_6H_5)$-$CH_2COOC_2H_5$ —Ethyl semicarbazinoacetate (1 mol) was heated in acetic ether solution for one hour with benzoyl chloride (1 mol), and to neutralize the hydrochloric acid liberated in the reaction, sodium bicarbonate (1 mol) was suspended in the acetic ether   The benzoyl derivative was isolated from the solution by concentrating this to a small volume and adding ether.   It is readily soluble in water, alcohol and acetic ether, and difficultly soluble in ether and benzene   It crystallizes from water in rectangular plates, which melt undecomposed at 172°

Calc for $C_{12}H_{15}O_4N_3$ C, 54 34, H, 5 66, N, 15 85   Found C 54 02 H, 5 82, N, 15 91

Conversion of the Benzoyl Derivative of Ethyl Semicarbazinoacetate to

3-Oxy-5-phenyltriazol-1-acetic Acid,
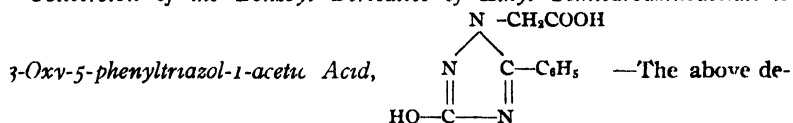
$$\begin{array}{c} N-CH_2COOH \\ \diagup \quad \diagdown \\ N \qquad C-C_6H_5 \\ \| \qquad \| \\ HO-C——N \end{array}$$ —The above described benzoyl derivative was converted into a triazol by heating with 10% potassium hydroxide solution for one-half hour, and the triazol was then precipitated by acidifying with hydrochloric acid [1]   It is moderately soluble in both alcohol and water, and can best be purified by crystallization from glacial acetic acid   On slowly heating it decomposes to a red liquid at 256°, beginning to melt at 253°

Calc for $C_{10}H_9O_3N_3$ C, 54 79 H, 4 11, N, 19 18   Found C 54 44, H, 4 37, N 18 94

Ethyl 3-Oxy-5 phenyltriazol-1-acetate —The triazol acid was esterified in the usual way by boiling with 6% alcoholic HCl for 3 hrs, the HCl was then neutralized with ammonia, the alcohol solution, filtered from the ammonium chloride, evaporated, and the residue taken up with water   On neutralizing the solution with ammonia, the ester separated out and was purified by crystallization from dilute alcohol   It melts undecomposed at 145°.

Calc for $C_{12}H_{13}O_3N_3$ N, 17 00   Found 17 30

Action of Phenyl Mustard Oil on Ethyl Semicarbazinoacetate.   1-Ureido-

3-phenyl-2-thiohydantoin,

$$\begin{array}{c} NH_2CONHN——CH_2 \\ | \qquad | \\ SC \qquad CO \\ \diagdown \quad \diagup \\ N—C_6H_5 \end{array}$$ —Phenyl mustard oil and
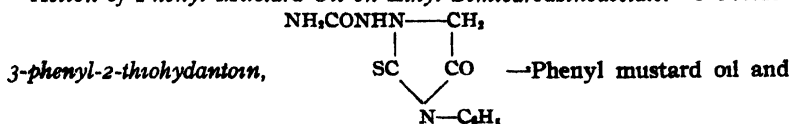
[1] Cf. *Ber.*, **29**, 1946 (1899), **33**, 1520 (1900), **45**, 30 (1912)

ethyl semicarbazinoacetate, in molecular proportions, were heated to boiling for one-half hour in glacial acetic acid solution. On cooling, the hydantoin crystallized out and was purified by recrystallizing from acetic acid and water. It is readily soluble in hot glacial acetic acid, and more difficultly soluble in alcohol and water. From the latter solvent it separates in thin plates with a pearly luster, which, on slow heating, melt with decomposition to a red liquid at 211°.

Calc. for $C_{10}H_{10}O_2N_4S$: C, 48.00; H, 4.00; N, 22.40; S, 12.80. Found: C, 47.53; H, 4.18; N, 22.61; S, 12.84.

Nitroso Derivative of Ethyl Semicarbazinoacetate, $NH_2CONHN(NO)$-$CH_2COOC_2H_5$.—The hydrochloride of ethyl semicarbazinoacetate and sodium nitrite in aqueous solution readily react to form a stable nitroso compound. This separates out, when the solution is concentrated, or can be extracted with ether or chloroform. The nitroso compound is soluble in the common solvents with the exception of petrolic ether, and can be purified by recrystallizing from benzene. It is of a light yellow color and gives the Liebermann reaction. Heated with 10% KOH, the nitroso compound decomposes with gas evolution. The substance begins to melt at 99° and decomposes completely at 102°

Calc. for $C_5H_{10}O_4N_4$: C, 31.58; H, 5.26; N, 29.47. Found: C, 31.67; H, 5.25; N, 29.79.

3,5-Dioxy-1,6-dihydro-1,2,4-triazine,

$$\begin{array}{c} NH \\ \diagup \diagdown \\ H_2C \quad\quad N \\ | \quad\quad\quad || \\ HO-C \quad\quad C-OH \\ \diagdown \diagup \\ N \end{array}$$

. *Sodium Salt.*—
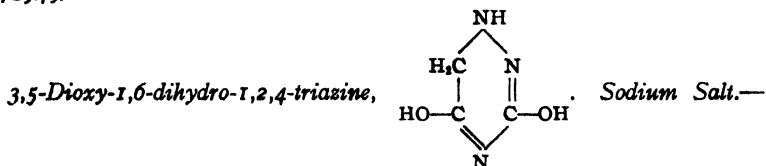
When one mol of sodium ethoxide in alcohol is added to an alcoholic solution of ethyl semicarbazinoacetate, there results an immediate precipitation of the above triazine salt. For analysis the salt was boiled with absolute alcohol and washed with ether.

Calc. for $C_3H_4O_2N_3Na$: N, 30.65; Na, 16.79. Found: N, 30.44; Na, 17.05.

The free triazine may be prepared as follows, without isolating the sodium salt: After mixing the semicarbazino ester and sodium alcoholate in equimolecular amounts in alcohol, the calculated amount of standard HCl is added, the solution heated to boiling, and filtered. In this process only a small amount of the triazine passes into the alcohol. The triazine is next separated from admixed sodium chloride by carefully leaching out the salt with the least possible quantity of cold water. It can be purified best by recrystallization from water, in which it is readily soluble, and from which it crystallizes in prismatic plates of a pearly luster, melting undecomposed at 221°. It is very difficultly soluble in alcohol,

and insoluble in the other common organic solvents.   A solution of the triazine decolorizes bromine water instantaneously.

Calc. for $C_3H_4O_2N_3$: N, 36 52   Found: N, 36.49.

Preparation of Ethyl Semicarbazinopropionate, $NH_2CONHNHCH$-$(CH_3)COOC_2H_5$ *from Pyruvic Acid Semicarbazone*, $NH_2CONHN =$ $CH(CH_3)COOH$.— The pyruvic acid semicarbazone[1] used in this experiment was made in a yield of about 92% by allowing semicarbazide and potassium pyruvate to react in aqueous solution.   The reaction proceeds with a considerable generation of heat, and at its close the semicarbazone can be precipitated by adding the calculated amount of hydrochloric acid.   The reduction was carried out just as in the case of glyoxylic acid semicarbazone, according to the method of Darapsky and Prabhaker, and the esterification process used there was found available in this preparation.   The ethyl semicarbazinopropionate does not separate out as the hydrochloride, but is readily extracted from neutral solution with chloroform.   Only one trial was made in the working out of the above process for the preparation of ethyl semicarbazinopropionate, and this resulted in a yield of 46% of the theoretical.   In another experiment, the ethyl ester of pyruvic acid semicarbazone was reduced in boiling 80% alcohol with 5% sodium amalgam, according to the method of Kessler and Rupe,[2] and the reduction product isolated in the form of the ethyl ester as above.   This experiment gave a yield of 64% of the theoretical.   However, a further study of these reduction processes would be necessary in deciding the best method of making this semicarbazino ester.   There is no doubt that semicarbazinopropionic acid esters can be more conveniently prepared from pyruvic acid semicarbazone than by the original method of Thiele and Bailey.   The semicarbazinopropionic acid ethyl ester made as above was compared with a preparation made by the method of Thiele and Bailey, and the two samples were in every way identical. Further, the reaction products with benzyl chloride, phenyl mustard oil, and sodium alcoholate referred to in other parts of this article were made and found to agree with the description of these substances.   A nitrogen determination on ethyl semicarbazinopropionate, prepared by the new process, follows.

Calc. for $C_6H_{13}O_3N_3$: N, 24.00   Found: N, 24.12.

Nitroso Derivative of Ethyl Semicarbazinopropionate, $NH_2CONHN(NO)$-$CH(CH_3)COOC_2H_5$.—This nitroso compound was made similarly to the nitrososemicarbazinoacetic acid ethyl ester described above, and gives the Liebermann reaction.   It crystallizes from acetic ether in long, slender prisms of a light yellow color, is readily soluble in water and

[1] *Ann.*, 303, 87 (1898).
[2] *Loc cit.*

alcohol, and difficultly soluble in ether and benzene.   It melts with gas evolution at 134.5°.

Calc. for $C_6H_{12}O_4N_4$: C, 35.29; H, 5.88; N, 27.45.   Found: C, 35 51; H, 5.97, N, 27.31.

CHEMICAL LABORATORY,
UNIVERSITY OF TEXAS,
AUSTIN, TEXAS.

THE PREPARATION OF ACROLEIN.

BY EDGAR J. WITZEMANN
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Although numerous methods have been proposed for the preparation of acrolein, it has remained relatively difficult to obtain it pure and in large quantities.   The most practical method for obtaining pure acrolein hitherto has been the phosphoric acid method proposed by Nef,[1] used by McLeod,[2] and investigated in some detail by Bergh.[3]   More recently Wohl and Mylo[4] have described a method for preparing acrolein in which anhydrous magnesium sulfate was used as the catalyst.   However, the apparatus used by Wohl and Mylo is composed entirely of especially constructed parts so that the method, as described by them, cannot be used except after a large outlay in time and money for the construction of the apparatus.   The present note is an account of a much simpler way of using magnesium sulfate in an apparatus composed of ordinary stock materials.   The results obtained by this modification are not so good as the best results obtained by Wohl and Mylo, but the method, as described here, is much more available for ordinary use.

Before discussing the modification of Wohl and Mylo's method I wish to record my experience with the phosphoric acid method.   The apparatus used was essentially like that used by Bergh.   A three liter Kavalier round-bottom flask standing in a Babo funnel and heated by a ring burner was used instead of the iron retort employed by Bergh.   That is, the apparatus was like that in Fig. 1, except that there was no dropping funnel in the generator flask and that the thermometer was pushed down into the glycerol.

Using an apparatus arranged in this way, a charge of 500 g., consisting of 475 g. of commercial glycerol and 25 g. of a pure phosphoric acid (d. 1.7), regularly gave 40–45 (sometimes 50 g.) of very pure acrolein.   It is necessary to regulate the flame of the ring burner carefully because more

[1] *Ann.*, 335, 221 (1904).
[2] *Am. Chem. J.*, 37, 33 (1907).
[3] *J. prakt. Chem.*, [2] 79, 351 (1909).
[4] *Ber.*, 45, 2050 (1912).

tar and less acrolein are formed the higher the temperature is raised above the point necessary to maintain active distillation. This is usually about 220° during the first part of the distillation. The temperature must usually rise to about 240° as distillation progresses. The end point of the distillation is very definitely indicated by the fact that the tar suddenly begins to foam up and fill the flask. If the temperature has been properly regulated, the flame may be turned down when the foaming begins and the tar foam will only rise part way in the flask. But if the tar is too hot it will boil over and accomplish one of several things, the least of which is to fill the distilling tube and condenser with tar.

When amounts of phosphoric acid are used corresponding to between 3 and 4.5% of the reaction mixture, the acrolein distillate is somewhat heavier (50-55 g.) but the acrolein thus obtained is slightly inferior. The temperature of decomposition rises as the percentage of phosphoric acid is decreased.   .

It was thought that perhaps the yield could be increased by continuing the distillation after the foaming stage. It was possible to heat the tars after the foaming but the yields were not very markedly increased and the quality of the acrolein was reduced by the last runnings. Apparently, the subsequent heating only tends to further dehydrate the tar without producing additional amounts of acrolein.

Attempts were made to increase the yield by placing only 200 g. of the charge in the generator and dropping the other 300 g. into the generator flask through a separatory funnel during the distillation. This proved to be unsatisfactory, because the reaction mass was likely to foam up at any moment unless very closely watched, and the yield of acrolein was not improved.

The tars formed in this process are relatively easily soluble in 5-10% alkali solutions. The solubility diminishes as the degree of dehydration increases.

After having prepared about 1.5 kilos of acrolein in this way the method was abandoned in favor of the following:

Modification of Wohl and Mylo's Method.

The method of Wohl and Mylo[1] has but one defect and that is, it can only be used after a heavy outlay for special apparatus. The modification here described was made in an attempt to utilize magnesium sulfate as a catalyst under less expensive conditions. After some experimentation with the use of distilling tubes, etc., the apparatus of Bergh's phosphoric acid method was modified as shown in Fig. 1. A is a ring burner resting on an asbestos board supported by a large ring attached to the ring stand. B is a Babo funnel. C is a three liter round-bottom Kavalier long neck (about 12 cm.) flask connected by an ordinary glass tube con-

[1] *Loc. cit.*

nection to a short condenser. A short bent adaptor connects this with the first receiver (a one liter flask), which contains 100–125 g. of common salt and is immersed in boiling water. The bent glass connecting tube leading from D is constricted at its lower end and has a hole blown about
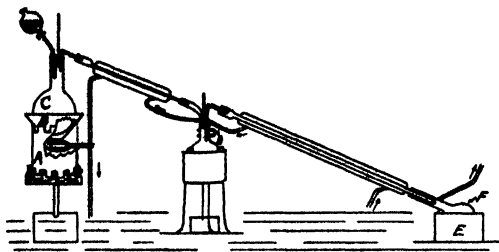
2.5 cm. from the lower end, in order to allow vapors to pass through it without forcing them through the water drops which continually fall from the lower end of this connecting tube. The receiver for the acrolein is kept immersed in an ice-water bath E. The

Fig 1

uncondensed acrolein vapors are disposed of by means of a rubber tube attached to the side arm of the receiving flask and which terminates in a good hood or outside of the building. The two ring stands supporting the condensers are not shown.

The hydrated magnesium sulfate was dehydrated by heating it with a good Bunsen burner in an iron pan. Dehydrated layers at least three-eighths of an inch thick were obtained. This material was broken up between the fingers into pieces varying from one-fourth to one-half inch in dimensions. The smaller particles and dust were carefully removed. One hundred and sixty grams of this were placed in the three liter flask. If dust and fine particles cover the bottom of the flask to any marked extent, the flask will probably be broken during the distillation, hence the care in removing the fine magnesium sulfate.

Just before beginning the distillation 200 g. of commercial glycerol are poured on the magnesium sulfate. The flask and contents are now warmed up fairly slowly by keeping the flame low at first. Meanwhile, the Bunsen lamp under D is lighted in order to heat the water bath to boiling. When acrolein begins to pass over into the second receiver (the water is held back by the salt in the first receiver) glycerol is slowly dropped into the generator through the dropping funnel. The glycerol must be added as fast as that already present is decomposed, but not much faster. If the glycerol is not added as fast as it is decomposed, the bottom of the flask burns dry and breaks, although the magnesium sulfate mass may be foaming actively and developing acrolein freely. The glycerol in the generator darkens in color and becomes more syrupy and tarry as the distillation proceeds. The rate of the tarring depends somewhat on the height of the flame on the ring burner. After having studied the reaction and learned the optimum conditions, I found that I could operate

with three sets of apparatus simultaneously and could thus obtain about 500 g. of very good acrolein in about five hours. The process requires very close attention, especially during the first few runs, but later on other work can be carried on easily.

Occasionally generator flasks break during distillation, but there is nothing to fear from this, since the odor given off is mostly that of hot sugar tar. This was a great surprise. It was expected that the odor of acrolein would be overpowering. Usually flasks are broken in this way because they are heated too rapidly at the beginning of the distillation. If the distillation has not progressed too far, so that the magnesium sulfate is not clogged with tar, the glycerol-soaked magnesium sulfate may be transferred to another flask and distillation continued. This was done a number of times.

Wohl and Wylo have suggested that the yield of acrolein might be increased, when distilling from a metallic retort containing the whole charge, by stirring the contents. From my experience in watching the operation in a glass flask it is apparent that the tar clogs up the pores and lumps of the magnesium sulfate; if this tar could be drained away from the catalyst the same catalyst could be used with much larger amounts of glycerol. This tar probably arises at first solely from acetol and it is possible that, as the amount of acetol tar increases, that either relatively more acetol is formed or that much of the acrolein is also resinified. At least it is certain that the yield in acrolein hour for hour diminishes somewhat as the distillation proceeds.

The acrolein as obtained in the second receiver is lemon-yellow in color and nearly always begins to polymerize at once. There are always a few grams of water in the bottom of each acrolein distillate. If this water is not removed, the polymerization does not proceed very far, so that the crude acrolein, if kept in a cool place, may be redistilled the next day without very great loss.

After having made some practive runs the following yields were obtained:

450 g. ⎫
460 g. ⎪ crude acrolein from 1800 g. gly- ⎫ When redistilled 320–60 g. of purified acro-
470 g. ⎬ cerol. Average yield 43%. ⎬ lein were obtained.
480 g. ⎭ ⎭

495 g. from 1850 g. glycerol............370 g. pure acrolein
547 g. from 2000 g. glycerol............425 g. pure acrolein.

The crude, moist acrolein began to boil at 51° and distilled over almost entirely between 52–54°; only a very small amount boiled between 54° and 58°, which was obviously due to the presence of water. Acrolein thus distilled polymerizes quite rapidly and should be agitated for a few minutes with granular calcium chloride until it clears up and then be

used at once. The calcium chloride must not be alkaline to litmus in aqueous solution, because such calcium chloride causes very rapid polymerization.

Under normal conditions the tar in the generator flask can be readily and quickly washed out with warm water. At other times there is a small amount of non-acid tar, which can be removed easily with the chromic acid cleaning mixture.

CHICAGO, ILL.

THE PHOSPHATES OF 2,3-DISTEARIN.[1]

BY R R. RENSHAW AND R. R. STEVENS
Received June 22, 1914.

Grun and Kade[2] have recently described a number of distearyl phosphates obtained by the action of phosphoric anhydride on 2,3-distearin. It would appear that the publication of their researches was delayed and that their results were obtained, in part at least, as early as 1910. We also began the study of the phosphatization of distearin in the summer of 1910, but our object was to obtain a definite substance and not *per se* to study the interaction of phosphorus pentoxide and distearin. Our investigation is not as complete as that of Grun and Kade, and we bring up no question of priority. There are, however, certain similarities and differences in our results which we think desirable to indicate at this time.

Under certain conditions, Grun and Kade obtained the mono-2,3-distearyl glyceryl phosphate and from the decomposition of this, by standing or by recrystallization from alcohol, ether or ligroin, they seem to have obtained primary, secondary, tertiary and quinquenary esters of o-phosphoric acid. Suggesting as probable, the intermediate formation of metaphosphates, they propose the following scheme to represent the decomposition, where R represents the distearyl radical:

$$RH_2P_2O_7 \longrightarrow RH_2PO_4 \longrightarrow R_2HPO_4 \longrightarrow R_3PO_4 \longrightarrow R_5PO_5$$

That is, for instance, the primary distearyl glyceryl phosphate breaks down in part into distearin and phosphoric acid and the distearin formed reacts with some of the undecomposed primary phosphate to form the secondary phosphate, and similar reactions yield the tertiary and quinquenary phosphates. The evidence offered seems to be sufficient with the possible exception of the quinquenary phosphate.[3]

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[1] Presented at the 49th General Meeting of the Am. Chem. Soc., Cincinnati, Ohio, April 8, 1914.

[2] *Ber.*, 45, 3358.

[3] In connection with this, it may be recalled that Grun himself has shown that diglycerides form very stable addition products with the fatty acids, as for instance, dimyristin forms $C_3H_5(OH)(OCOC_{13}H_{27})_2 + 2HOOCC_{13}H_{27}$. The phosphorus content of the quinquenary ester and of such an addition product of the tertiary phosphate with four molecules of stearic acid differ within the allowable analytical error.

Both from experimental data and from analogy with the reversibility of the reaction of concentrated sulfuric acid and stearic acid on mono and distearin, the decomposition proposed by Grun and Kade was viewed with surprise by the present authors. Our results show clearly the tendency of the phosphates to hydrolyze, forming products poorer in fatty acid and richer in phosphorus rather than the reverse as found by Grun and Kade.

We have confirmed the work of Grun and Kade and of Hundeshagen[1] on the preparation of the primary o-phosphate of 2,3-distearin. In addition we have isolated salts of a pyrophosphate which appears to be

$$
\begin{array}{l}
\mathrm{CH_2-O-COC_{17}H_{35}} \\
\quad | \qquad\qquad\quad O \\
\mathrm{CH-\,-O-P\diagup}\!\!\!\diagdown\mathrm{ONa} \\
\quad | \qquad\qquad\quad O \\
\mathrm{CH_2-O-P\diagup}\mathrm{ONa} \\
\qquad\qquad\quad\diagdown O
\end{array}
$$
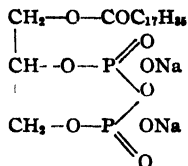
This was obtained in an attempt to simplify the process for the separation of the primary distearyl glyceryl phosphate. A typical example of the procedure follows: 2.5 g. of distearin and 1.3 g. of phosphorus pentoxide were heated for an hour at 100° with constant stirring. The reaction product was cooled, pulverized and sifted with stirring into a saturated solution of sodium hydrogen carbonate. The brownish, granular material separating in the bottom of the beaker was filtered, washed with water and extracted with acetone to remove stearic acid and distearin. About one-fourth of the residue from the acetone extraction was soluble in boiling benzene. The remainder, insoluble in benzene, was boiled with water, and its concentrated aqueous solution precipitated with acetone. In the boiling stearic acid was split off. The combined soluble products were purified by dissolving in benzene and precipitating with acetone, and finally recrystallizing from petroleum ether. It separated from this solvent in prismatic plates melting at 167–8° (uncor.). The yield was about 0.47 g.

Calc. for $C_{41}H_{40}O_9P_2Na_2$: P, 11.39%; stearic acid, 52.2%. Found: P, 11.51%, 11.43%; stearic acid, 51.86%.

This sodium salt dissolves in hot water, giving a solution resembling that of soap. It is soluble in hot benzene and in petroleum ether and is nearly insoluble in acetone.

A silver salt was obtained by precipitating a concentrated solution of the sodium salt with silver nitrate. It melts at 147.5° (uncor.) and readily darkens.

Calc. for $C_{41}H_{40}O_9P_2Ag_2$: Ag, 30.23%. Found: Ag, 30.19%.

Insoluble barium and calcium salts were also obtained.

[1] *J. prakt. Chem.*, **28**, 232.

No attempt was made to investigate further the product insoluble in benzene.

WESLEYAN UNIVERSITY AND IOWA STATE COLLEGE.

OIL OF OCYMUM PILOSUM ROXB.

BY KSHITIBHUSAN BHADURI.
Received June 8, 1914.

The botanical characteristics of *Ocymum Pilosum, Roxb.* are as follows: Shrubby, branches four-sided, and furrowed. Leaves, ovate oblong, cerrat. Bractes petioled, sub-orbicular, hairy; upper tip of the calyx orbicular and hairy, with corrolla twice its length.

The seeds when steeped in water swell into a jelly, which is used medicinally by the natives of India.

The plant has a very strong odor of the oil, which is found in the whole of it as well as in the seeds; but, when the latter are dried, no oil can be got from them by distillation. This may be due to either of the two causes, *viz.*, the oil is extremely volatile and when the plant dries it volatilizes, or in the course of drying, the oil resinifies and, as such, it cannot be obtained by distillation.

The percentage of oil in the green seeds is higher than in that of the leaves. The oil has been obtained by the author by distillation at the laboratory, the total volume obtained being very small. The season being over, it was not possible to obtain a fresh supply of the plant. It is hoped, however, that a good quantity of oil may be obtained the coming season, when the results of further investigation will be communicated.

To obtain the oil, the whole plant, as cut down, can be at once submitted to steam distillation. The whole of the oil comes over within a very short time, about half an hour being sufficient for this purpose. It is a very thin mobile liquid with a pale yellow color. When left exposed to the atmosphere part of it volatilizes and a resinous mass remains. The odor is almost identical with that of lemon-grass oil.

Experimental.

The specific gravity as determined with a pycnometer, was found to be 0.8872 at 25.5°. The refractive index, as determined in a Pulfrich's refractometer, is 1.4843 or 40° 12' at 24.5°. The oil is laevo-rotatory, the optical rotation being —3.7° in a tube one decimeter long. The specific rotatory power $[\alpha]_D$ is, therefore, —4°10'14" at 24.5°.

Generally, Basil oils contain methyl-chavicol, which gives a blue coloration with ferric chloride.[1] When ferric chloride solution (neutral) was

[1] *Richter's Organic Chemistry*, p. 269.

added to an alcoholic solution of this oil no coloration was produced, proving the absence of this compound. When a few drops of the oil were shaken with a neutral solution of sodium sulfite and phenolphthalein, a pink coloration was produced, showing that aldehydes were present. From the resemblance of its odor to that of lemon-grass oil it was suspected to contain citral. To prove it, a drop of the oil was shaken with a solution of mercuric chloride in 25% sulfuric acid when a red coloration was produced. The presence of this substance, as well as that of citronellal, was proved by preparing condensation products with pyruvic acid and β-naphthylamine, separating them by fractional crystallization and determining their melting points.

On adding a strong solution of iodine in potassium iodide a pasty mass with green lustrous scales was produced, proving the presence of cineol. When two drops of the oil were gently heated on a porcelain basin with one drop of strong hydrochloric acid and one drop of a strong solution of ferric chloride, it developed a rose color, showing that limonene is present. This substance was also isolated from the oil and its properties were found to be identical with that of a sample of limonene.

Here it may be mentioned that whenever the oil is treated with a strong mineral acid it developed a camphor-like odor. It does not contain any free acid. It was found that 10% of the oil was absorbed when shaken with a 5% solution of caustic potash. It contains a very small quantity of thymol. The major portion of the oil distilled between 205-230° C.

For the estimation of citral and citronellal the method of Teimann was used. 5 cc. of the oil were shaken in a Hirschsohn flask with a solution of 19 g. of sodium sulfite and 7 g of sodium bicarbonate for several hours, and allowed to stand, after adding water to make the unabsorbed portion collect in the neck. The volume of this was found to be 1.25 cc., or 75% by volume of the oil were aldehyds. The aqueous liquid was transferred to a larger flask and shaken with ether to extract the non-aldehydic constituents in it. The citral was liberated by the addition of a solution of caustic potash previously saturated with ether. A layer of ether was poured into the flask and the alkali solution added so that the citral was taken up by it as soon as liberated. The ethereal layer was taken in a weighed basin and the ether allowed to evaporate. From the difference in weight of these two we get the weight of citral and subtracting this from that of the total aldehydes we get the percentage of citronellal. The weight of citral found was 1.8 g. This is equal to 2.05 cc., or 41% by volume. Hence the percentage of citronellal is equal to 75-41 or 34.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA,
INDIA.

STUDIES ON WATER DRINKING. XVIII. ON THE RELATION BETWEEN WATER INGESTION AND THE AMMONIA, PHOSPHATE, CHLORIDE AND ACID EXCRETION.

BY D W. WILSON AND P. B HAWK.

In the course of a former investigation carried out by one of us[1] it was demonstrated that the ingestion of water was followed by an increased excretion of urinary ammonia and that the extent of this increase for any given subject was directly proportional to the volume of water ingested. The actual increase in the ammonia output varied, however, for different individuals. The relation between the water ingestion and the increased ammonia output as determined for the two subjects of that experiment was as follows.

	Subject W		Subject E	
	Expt I Copious H_2O Moderate H_2O	Expt II NH_3 inc (cop) $\overline{NH_3 \text{ inc}}$ (mod)	Expt III Copious H_2O Moderate H_2O	Expt IV NH_3 inc. (cop) $\overline{NH_3 \text{ inc}}$ (mod)
	1 1 81	1 . 1 75	1 2 66	1 2 54

The above data indicate that when the water ingestion of Subject W was increased from a value of 1 to a value of 1 81 that the ammonia excretion simultaneously rose from a value of 1 to a value of 1.75. In the case of Subject E the water and ammonia ratios were 1 . 2 66 and 1   2 54. The increased output of ammonia under the influence of water ingestion was interpreted as indicating a stimulation of gastric secretion.

In order to make a further study of the water-ammonia relationship, using other subjects, the present investigation was planned. The relationship of the ammonia output to the urinary chloride, phosphate and acid excretion was also included.

The general plan of the experiment was similar to that of other experiments previously reported.[2,3] Two normal young men served as subjects. The diet was simple in character and uniform from day to day. The actual daily diet as fed was as follows·

Graham crackers	300 grams	Peanut butter	45 grams
Milk (whole)	1200 cc	Water (distilled)	300 cc
Butter...	75 grams		

The experiment was divided into five periods as follows· preliminary (3–5 days), moderate water drinking (10 days), intermediate (5 days), copious water drinking (5 days), final (5 days).

[1] Wills and Hawk, This Journal, 36, 158 (1914)

[2] Mattill and Hawk, Ibid., 33, 1978 (1911)

[3] Fowler and Hawk, Exp. Med., 12, 388 (1910).

During the preliminary, intermediate and final periods Subject C ingested 400 cc. water per day between meals, whereas Subject V drank 600 cc. During the moderate water drinking period each subject took 500 cc. water additional at each meal. Thus the total daily water ingestion of C during this period was 2200 cc., whereas V drank 2400 cc. In the period of high water intake each subject drank 850 cc. water at each meal. This increase made the daily water ingestion of C 3250 cc., whereas that of V was 3450 cc.

Ammonia and acidity were determined by Folin's methods. The phosphates were determined by the uranium method, whereas chlorides were estimated by the Dehn-Clark procedure.[1]

Discussion.

Chlorides and Phosphates.—The excretion of chlorides showed small variations. Both subjects excreted less during the water periods and showed a lower output with moderate than with copious water ingestion. The averages for the preliminary period (6.6 and 6.45 grams) indicate a low chloride ingestion, which may account for the small variations observed in the different experimental periods. With a low chloride intake there would be less liability of retention and flushing out of the tissues with the increased water ingestion. In fact the data indicate a reverse tendency. On the first day of each period of moderate and copious water ingestion there was a retention instead of a loss. This undoubtedly was due to the efforts of the body to maintain the normal osmotic pressure in its various fluids. In most cases there was a marked retention of water, and as distilled water was ingested, a considerable retention of inorganic salts was necessary. The phosphates were excreted in normal amounts in order to eliminate acids formed from metabolic procedures, so that the first source of material for maintenance of osmotic pressure would be the ingested chlorides.

The most marked example of the chloride retention was in the case of Subject V. On the 1st day of the intermediate period the chloride output was 8.2 g., whereas on the two following days in which copious volumes of water were ingested the chloride sank to 4.7 and 4 0 g., respectively, values only about 50% as great as that previously obtained. The intermediate period showed an increased chloride output due to the loss of water when the water ingestion was decreased. The use of distilled water with a low ingestion of inorganic salts may easily account for the lack of greater variations in the chloride output than those observed.

Ammonia and Acidity.—The variations in the ammonia output, as influenced by the ingestion of water are readily apparent from an examination of the tables. Increased water ingestion was followed by an in-

[1] See Hawk's "Practical Physiological Chemistry," fourth edition, 1912, p. 417.

creased excretion of urinary ammonia. Subject V gave a normal ammonia value of 0.26 g. in the preliminary period which value was increased to 0.32 g. when a moderate increase in the water ingestion was made. The maximum ammonia value was 0.33 g. and was obtained during the copious water period. The ammonia data of Subject C showed greater variations, but with the same general tendency. The preliminary period gave an average ammonia excretion of 0.29 g., which underwent an increase of 0.37 g. during the period of moderate water intake. The average of the intermediate period was slightly lower than that of the preliminary period (0.26 g.), but rose again upon copious water ingestion to 0.34 g., a value which was somewhat lower than the value yielded by this subject upon the ingestion of moderate quantities of water. The final period gave a minimum average of 0.25 g.

Subject C showed an increased excretion of acid and phosphates during the water drinking period with maxima during the moderate water ingestion. Subject V showed a decreased excretion of both constituents in both cases.

The increased excretion of ammonia as observed with both subjects and the increased excretion of acids and phosphates in the case of Subject C indicate to us an increased cell metabolism, causing a formation of acid products which are partly neutralized by ammonia formation and partly cause increased acid phosphates in the urine. Various experiments in this and other laboratories have shown increased total nitrogen excretion, and one of us has recently observed[1] an increased neutral sulfur output after ingestion of considerable quantities of water. It has been suggested that neutral sulfur is a product of cellular metabolism. The increase of total nitrogen and neutral sulfur substantiates our assumption that the observed increased excretion of ammonia, phosphates and increased urinary acidity is due to stimulated cell metabolism caused by ingestion of considerable quantities of water.

A complication which undoubtedly makes less apparent any variations which are produced, is the necessity of maintenance of osmotic pressure by the body. This calls for considerable amounts of dissolved solids drawn from the tissues by the distilled water ingested. As inorganic salts are the most efficient means of developing osmotic pressure, as well as the most available, they would be most in demand and thus cause a retention of the constituents with which we are dealing. This retention undoubtedly occurs in all the water periods of the experiment and is sufficient in the case of Subject V to mask any tendency toward increased excretion of the acid phosphates. The same consideration probably explains why the values (NH₃, acidity and phosphates) for the copious water periods were lower than the values for the moderate water periods.

[1] Fowler and Hawk, Unpublished.

The retention of even small volumes of distilled water by the body would call for a marked retention of inorganic salts   For example, a retention of nearly 3 g. of inorganic salts, calculated as NaCl, would be necessary to render 300 cc of distilled water isotonic   Calculated as

SUBJECT C

Day		Urine Volume Cc	NH₃ N Grams	Acidity Cc $N/10$ NaOH	P₂O₅ Grams	Chloride. Grams NaCl
			Preliminary			
4		720	0 29	252 6	1 50	6 78
5		620	0 26	235 4	1 94	6 57
6		615	0 31	300 2	1 93	6 57
	Average	651	0 29	262 7	1 79	6 64
			Moderate water			
7		995	0 38	324 7	1 88	5 44
8		1465	0 37	324 4	2 24	6 60
9		1215	0 41	343 8	1 99	5 96
10	.	1620	0 36	281 0	2 24	5 98
11		2040	0 38	242 9	1 97	6 31
12		2050	0 37	242 2	1 97	6 04
13		1800	0 35	265 7	1 97	6 31
14		2230	0 34	224 2	1 93	6 54
15		2330	0 38	346 0	1 90	7 14
16		1930	0 38	280 5	1 98	6 29
	Average	1768	0 37	287 5	2 01	6 26
			Intermediate			
17		860	0 29	219 6	1 84	6 64
18		675	0 28	289 3	1 88	5 92
19		700	0 28	241 8	1 88	5 96
20		770	0 24	200 6	1 88	8 00
21		710	0 19	182 9	1 86	7 30
	Average	743	0 26	226 8	1 87	6 76
			Copious water			
22		2900	0 33	253 4	2 09	6 34
23		2670	0 36	234 5	1 61	5 38
24		3360	0 35	244 9	1 97	6 97
25		3210	0 35	255 8	1 96	6 61
26		3300	0 32	228 6	1 86	7 41
	Average	3088	0 34	243 4	1 90	6 54
			Final			
27	.	920	0 23	233 5	1 70	6 77
28	.	820	0 26	259 5	1 75	5 78
29		835	0 26	279 1	1 88	6 13
30		810	0 25	292 7	1 94	6 44
31		850	0 25	244 4	1 94	7 32
	Average	847	0 25	261 8	1 84	6 49

Subject V.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.

Preliminary.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.
4	740	0.22	254.9	1.72	5.78
5	1425	0.27	219.3	1.95	8.99
6	890	0.31	268.0	1.93	6.39
7	665	0.26	265.3	1.89	5.64
8	690	0.24	248.6	1.84	5.49
Average	882	0.26	251.2	1.86	6.45

Moderate water.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.
9	2110	0.31	258.9	1.77	5.07
10	2210	0.31	240.1	1.88	6.06
11	1620	0.34	245.0	1.82	5.70
12	1970	0.21	159.6	1.02	6.73
13	2380	0.33	204.7	1.45	6.65
14	2550	0.29	219.4	1.89	6.72
15	2165	0.38	238.2	1.66	5.72
16	2635	0.34	201.6	1.43	6.73
17	2205	0.36	245.6	1.47	5.76
18	2410	0.29	216.1	1.64	5.98
Average	2226	0.32	222.9	1.60	6.11

Intermediate.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.
19	1230	0 25	201.6	1.56	7.26
20	1025	0.26	240.9	1.78	5.88
21	1000	0 25	240.4	1.71	6.40
22	1195	0.24	220.9	1.96	7.23
23	1670	0.23	233.7	1.92	8.21
Average	1224	0.26	229.3	1.79	7.00

Copious water.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.
24	3400	0.35	224.9	1.65	4.70
25	3140	0.35	226.0	1.47	4.02
26	3600	0.31	207.1	1.77	6.91
27	3860	0.33	199.2	1.63	8.38
28	3660	0.33	212.1	1.67	6.91
Average	3532	0.33	213.8	1.64	6.18

Final.

Day.	Urine. Volume. Cc.	NH₃ N. Grams.	Acidity. Cc. N/10 NaOH.	P₂O₅. Grams.	Chloride. Grams. NaCl.
29	920	0.25	232.2	1.63	6.12
30	1240	0.27	223.5	1.82	6.69
31	835	0.28	271.7	1.72	5.25
32	815	0.23	217.6	1.75	5.53
33	1010	0.22	208.7	1.84	6.89
Average	964	0.25	230.7	1.75	6.10

phosphates, the value would be higher. A retention of double that volume was indicated by variations in body weights of the subjects in the different periods.

Considering the variations in the excretion and retention which would be caused by the variations in the water content of the body, the small differences which we have obtained in our experiments are much more significant, for our increases in ammonia, phosphate and acid output have been evident in spite of the tendency to retention and obscurity. In other experiments in this laboratory, where ordinary tap water has been used, the variations were much more pronounced. This was undoubtedly favored by. the presence of salts in the water which made it less necessary for the body to supply the necessary material for development of sufficient osmotic pressure.

It will be observed that the increase in urinary ammonia which followed the increased water intake by the subjects of these tests was not proportional to the volume of water ingested. This lack of relationship is easily explained on the basis of certain experiments now in progress by one of us.[1] In the tests mentioned the introduction of distilled water into the empty stomach causes an increased flow of gastric juice but the increased flow is, in some cases at least, in no way proportional to the volume of water introduced into the stomach. Inasmuch as we believe the ammonia output, under such conditions, is regulated to a large degree by the amount of acid entering the intestine, the non-parallelism of the water intake and the ammonia output may be logically explained.

PHILADELPHIA, PA.

STUDIES ON WATER DRINKING. XIX. INTESTINAL PUTREFACTION AS INFLUENCED BY THE INGESTION OF SOFTENED AND DISTILLED WATERS.

BY C. P. SHERWIN AND P. B. HAWK.

Investigations already reported by one of us[1] indicated that the drinking of copious (1000 cc.) or moderate (500 cc.) volumes of water with meals decreased intestinal putrefaction as measured by the urinary indican output, and that copious water drinking caused a more pronounced lessening of the putrefactive processes than did the moderate water drinking. Softened water was employed in the experiments in question. In the present instance the influence of both distilled and softened water was studied.

The investigation here reported embraced two experiments, young men

[1] Rehfuss, Bergeim and Hawk, Unpublished.

serving as subjects in each instance. A general description of the subjects, diets, etc., used in the two experiments will be found in other connections.[2,3]. The indican determinations were made by Ellinger's[4] method as modified by Maillard.[5] The former method has already been given in another connection.[1] The modification consists in washing the chloroform extract with an equal volume of o.1% sodium hydroxide and removing the adherent alkali by careful washing with distilled water. From this point the Ellinger procedure is followed. The ethereal sulfates were determined by Folin's procedure.

Experimental.

First Experiment.—This experiment was divided into three periods, a preliminary period of three days, a water period of five days, and a final period of two days. A uniform diet was ingested throughout the study, with the exception that the water ingestion of each day of the water period was increased by three liters, taken at meal time, one liter with each meal. The water was a freshly softened water. Data from this experiment are given in Table I.

TABLE I.

Day.	Urine. Cc.	KMnO₄ soln. in titrating 40 cc. of the clarified sample. Cc.	KMnO₄ soln. used to titrate the entire urine volume. Cc.	Indican output per day. Mg.
Preliminary Period (3 Days).				
1	830	5.90	135.3	35.6
2	920	6.70	168.5	44.1
3	880	4.50	107.8	28.4
Average	877	5.70	137.2	36.0
Water Period (5 Days).				
4	3440	3.50	112.8	29.7
5	3840	3.60	125.8	33.1
6	3670	2.90	96.8	25.4
7	3610	3.05	99.9	26.3
8	4020	2.85	104.2	27.4
Average	3716	3.18	107.9	28.3
Final Period (2 Days).				
9	1390	6.65	290.9	76.5
10	885	9.83	237.6	62.5
Average	1237	8.24	264.2	69.5

An examination of the last column in Table I will serve to show that the average output of indican for the preliminary period was 36.0 mg. per day. During the five-day interval of high water ingestion this value was reduced to a daily average of 28.3 mg. It is evident, therefore, that the drinking of one liter of softened water with each meal for a period of five

days caused a lessening of the processes of intestinal putrefaction as measured by the urinary indican excretion.

Second Experiment.—This experiment was divided into five periods, a preliminary period of 6-8 days, a moderate water period of ten days, an

TABLE II.—INDICAN AND ETHEREAL SULFATES.
Subject C.

Day of exp.	Cc urine.	Specific gravity.	Ethereal sulphates Mg.	Indican Mg.	$\frac{SO_3}{Indican-SO_3}$
Preliminary Period.					
5	620	1.032	153.8	27.2	17.73
6	615	1.033	153.8	23.4	20.62
Average	618	1.033	153.8	25.3	19.17
Moderate Water Period.					
1	995	1.019	24.3	20.2	3.78
2	1465	1.014	16.9	24.4	2.18
3	1215	1.015	98.1	31.2	9.86
4	1620	1.012	142.6	15.4	29.16
5	2040	1.010	172.6	28.1	19.24
6	2050	1.009	108.9	9.2	37.04
7	1800	1.011	137.5	5.3	80.99
8	2230	1.010	78.0	29.6	8.29
9	2330	1.009	171.6	22.2	24.20
10	1930	1.010	206.0	27.9	23.17
Average	1767	1.012	115.6	21.3	23.79
Intermediate Period.					
1	860	1.023	170.9	22.3	24.04
2	675	1.038	130.1	27.3	14.97
3	700	1.030	76.9	26.6	9.07
4	770	1.028	69.8	16.1	13.56
5	710	1.027	118.5	13.8	26.96
Average	743	1.029	113.2	21.2	17.72
Copious Water Period.					
1	2900	1.008	128.0	14.9	26.99
2	2670	1.007	155.7	13.8	35.34
3	3360	1.007	174.9	16.8	32.71
4	3210	1.007	154.0	15.3	31.64
5	3300	1.006	152.8	16.8	28.53
Average	3088	1.007	153.1	15.5	31.04
Final Period.					
1	920	1.023	219.2	20.6	33.37
2	820	1.024	183.8	24.6	23.45
3	835	1.024	209.6	30.1	21.85
4	810	1.026	132.2	24.6	16.89
5	850	1.026	139.9	22.2	19.74
Average	847	1.025	176.9	24.6	23.06

intermediate period of five days, a copious water period of five days and a final period of five days. Two subjects were employed and the water used was distilled water. A uniform diet was fed and was supplemented by an increase of 500 cc. in the water ingestion of each meal of the moderate

TABLE III.—INDICAN AND ETHEREAL SULFATES.

Subject V.

Day of exp.	Cc. urine.	Specific gravity.	Ethereal sulfates. Mg.	Indican. Mg.	SO₃ / Indican—SO₃.
		Preliminary Period.			
7	665	1.029	...	64.7	...
8	690	1.029	...	79.7	...
Average	677	1.029	...	72.2	...
		Moderate Water Period.			
1	2110	1.008	91.2	60.6	4.74
2	2210	1.009	81.5	62.2	4.12
3	1620	1.012	112.1	53.7	6.56
4	1970	1.008	221.4	70.8	9.82
5	2380	1.008	118.5	89.6	4.14
6	2550	1.008	235.5	83.1	8.88
7	2165	1.008	247.8	90.6	8.57
8	2635	1.007	121.1	90.3	4.21
9	2205	1.010	182.0	89.3	6.40
10	2410	1.007	200.0	93.6	6.72
Average	2254	1.009	154.4	79.2	6.04
		Intermediate Period.			
1	1230	1.016	66.8	71.5	2.92
2	1025	1.020	135.0	81.3	5.21
3	1000	1.020	227.3	78.9	9.04
4	1195	1.017	179.1	81.6	6.90
5	1670	1.015	180.1	73.6	7.69
Average	1224	1.018	157.7	77.4	6.35
		Copious Water Period.			
1	3400	1.005	322.2	68.5	14.75
2	3140	1.005	110.7	74.0	4.68
3	3600	1.006	211.1	60.8	10.89
4	3860	1.006	165.1	76.9	6.75
5	3660	1.006	184.5	64.7	8.95
Average	3532	1.006	198.7	64.9	9.20
		Final Period.			
1	920	1.021	207.9	99.1	6.59
2	1240	1.017	203.8	99.8	6.40
3	835	1.024	151.5	95.3	4.99
4	815	1.022	170.9	84.5	6.34
5	1010	1.020	156.0	85.0	5.74
Average	964	1.021	178.0	92.7	6.01

water period and an increase of 850 cc. in the water ingestion of each meal of the copious water period.

The data from this experiment are given in Tables II and III. From an examination of Table II it will be seen that subject C excreted 25.3 mg. of indican per day during the preliminary period. The ingestion of a moderate volume (500 cc.) of water at each meal reduced this indican value slightly (21.3 mg.), whereas the ingestion of a larger volume of water (850 cc.) at each meal caused a more pronounced drop in the indican value, as is shown by an average daily output of 15.5 mg. for the copious water period. An examination of Table III will show that the minimum indican value for subject V was also secured during the period of high water ingestion. In each instance the water evidently caused a decrease in the putrefactive processes.

It is interesting that, coincidently with the most pronounced *decrease* in the excretion of indican, *i. e.*, during the period of copious water intake, there was a correspondingly pronounced *increase* in the ethereal sulfate output. This failure of the indican and total ethereal sulfate values to run parallel has been previously discussed by ourselves[1],[7] and others.[6] Such observations furnish strong evidence in favor of the current belief that indican has a different origin from the other ethereal sulf ue.

Discussion.

The data herewith submitted indicate that the ingestion of water, either distilled or softened, is accompanied by a decrease in the processes of intestinal putrefaction. The examination of the stools from these same subjects has shown that the output of fecal bacteria was also decreased during the periods of high water intake.[2],[3] The logical conclusion, therefore, would appear to be as follows: The ingestion of the large volume of water stimulated the flow of a gastric juice of increased acidity.[8],[9],[10] The acid chyme upon its entrance into the intestine inhibited the activity of the indole-forming bacteria thus causing a decreased output of indol and consequently a decreased indican excretion. The fact that a high water intake is accompanied by better digestion and absorption of the ingested protein[2],[11] would cause the protein residues in the intestine to be lessened in amount, thus reducing the quantity of material available for the growth and development of the bacteria in question. Hence the lowering of the putrefactive processes would naturally be accompanied by a decrease in the development of the intestinal flora and a consequent drop in the fecal bacteria values.

So far as the data from the present investigation are concerned, it is evident that distilled and softened water are equally efficient in causing a decrease in the processes of intestinal putrefaction.

Many objections have been raised against the practice of drinking distilled water. Most of these objections we believe to have but slight

foundation in fact. According to Findlay[12] the ingestion of distilled water is followed by the swelling of the surface layers of the epithelium of the stomach, due to the passage of water into the cells because of the difference in osmotic pressure. The cells finally die, are cast off and catarrh of the stomach may result. Koeppe[13] and Harlow[14] have expressed somewhat similar ideas, whereas Nocht[15] and Winkler[16] cite instances showing prolonged drinking of distilled water to have been unaccompanied by any serious consequences. Recently, Oehler[17] claims to have produced hemoglobinuria in white mice by the introduction of distilled water into the stomach. We are rather skeptical as to the possibility of producing hemoglobinuria in any such manner. That hemoglobinuria will follow the introduction of distilled water into the circulation is well known. It is, however, rather surprising that the introduction of distilled water into the stomach should cause such a phenomenon. As soon as distilled water reaches the stomach it ceases to be distilled water, due to the fact that it at once takes unto itself various electrolytes which are present in the food and digestive juices.

We have shown that even the prolonged ingestion of large volumes of distilled water over a long period of time was not accompanied by the production of any observable catarrhal affection of the gastric mucosa. This observation was made in connection with a fasting dog which received 700 cc. of distilled water daily for a period of 104 days.[18] No evidences of catarrh of the stomach were apparent. Certainly, if distilled water was able to produce this type of disorder, here was an excellent opportunity. There was no food ingested for 104 days and consequently no electrolytes from this source to lessen the harmful (?) influence of distilled water to which various authors have referred.

Conclusions.

Both softened and distilled water when taken with meals in volumes ranging from 500 cc. to 1000 cc. have a tendency to cause a decrease in the putrefactive processes in the intestine as indicated by the urinary indican excretion.

The non-parallelism of the indican and total ethereal sulfate elimination was again observed.

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A PIPETTOMETER.

By W D Frost

Received June 16 1914

The pipettometer is a new piece of apparatus for measuring out precise amounts of fluids without the use of graduated pipets It was originally intended for work in the bacteriological laboratory but will, no doubt, be found of interest to those working in other laboratories such as those of chemistry, physics and medicine

It consists essentially of an upright graduated glass tube with an upper side arm to which, by means of a piece of rubber tubing ungraduated glass pipets may be readily attached At the lower end of this graduated tube, another tube is attached by means of a flexible rubber joint This tube has a bulb at the outer end and is so arranged that the bulb end can be readily raised or lowered The upright tube and this movable arm with bulb are partially filled with mercury The whole apparatus is supported on a wooden or metal frame which is so attached to a ring stand that its height can be varied By moving the bulb up or down, the height of mercury column in the graduated upright can be raised or lowered When the mercury is lowered in this tube, the pipet draws up the fluid into which its tip is immersed and when it is raised the fluid is forced out The amount of fluid taken up or discharged is measured by reading the position of the mercury in the graduated upright

The details of the construction and the use of the pipettometer can best be understood by reference to the accompanying figure

A is the wooden or metal support with its short arm on the top and left *C*, while *B* is the longer arm on the right, hinged at the bottom The whole is supported on a ring stand, *D*, to which it is held by the screw clamps *ff* Mounted on this frame is the bent glass tube *abcd*, with a flexible joint at *c* and a bulb at *d*

When the arm *B* is moved up to position I, the mercury stands at 1 0, and when it is lowered to II the mercury stands at 0 A graduated pipet,

g, is attached at a and the arm B_a^v is raised to I. A vessel containing the fluid to be drawn into it is brought to the point of the pipet and the arm
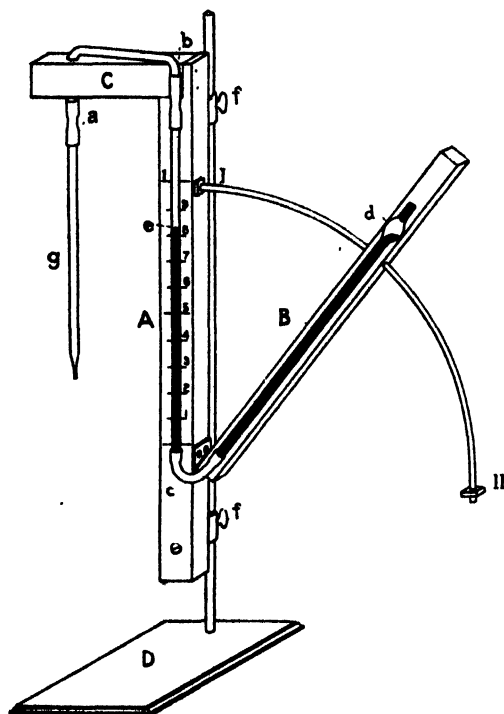
B is lowered to II. In this way, the fluid is drawn into the pipet g. It can then be discharged in whole or in part by slowly raising the arm B. The amount discharged is indicated on the scale.

The graduations on the scale must be carefully made. This can be done by drawing water into g and then discharging it and weighing it on a fine balance. In this way the 0.5 and 1 cc. points can be determined. It will be accurate enough for ordinary work to mark off the intervening points. At first thought it might be supposed that all that it would be necessary to do would be to put a carefully graduated pipet in the system between b and c but a little reflection will show that this would not be accurate, because the weight of the fluid in the pipet rarefies the column of air between the fluid in the pipet and of the column of mercury, so that not quite the proper amount of fluid is taken up. When, however, the graduations are once obtained, it is then possible to measure any fluid very accurately if it has practically the same specific gravity as the fluid used to make the graduations.

The apparatus was originally made to handle 1 cc. lots and it was found that, with a little practice, measured quantities could be handled as quickly and accurately as with graduated pipets.

The tube bc can be replaced by a very small tube, in which case hundreths of a cubic centimeter can be easily measured. Or it can be replaced by tubes of greater capacity which arrangement makes it convenient for measuring amounts of 10 cc. or more.

It can be used for handling poisonous or infectious material with great satisfaction, and can, furthermore, be readily used to calibrate pipets.

MADISON, WIS.

[CONTRIBUTION FROM THE WOLCÒTT-GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

AN ADVANTAGEOUS FORM OF STILL FOR THE EXACT MEASUREMENT OF BOILING POINT DURING FRACTIONAL DISTILLATION.

BY THEODORE W. RICHARDS AND FREDERICK BARRY
Received June 8, 1914

In the course of a recent investigation on the heats of combustion of liquid hydrocarbons, it was needful to prepare certain of these substances in a very high degree of purity, and at the same time in considerable quantity. For this work it was necessary to determine exact boiling points, and an advantageous form of still was devised, which proved itself, especially in this respect, more efficient than any of the apparatus now in common use. This still, because of its simplicity and usefulness, and because it does not appear to have been proposed before, seems to the authors to merit separate brief description.

In the accompanying drawing, two forms of the instrument are shown. Fig. 1 represents the type first constructed: of this the other is a simple modification. A glance will show the immediate purpose of the device. The still was designed to hold a sensitive Beckmann thermometer, so that very small fluctuations in the boiling point of the liquid under examination could be accurately observed, and the boiling point of the purest distillate precisely determined by a comparison with a standard vapor of neighboring known boiling point. The still not only served this purpose admirably, but proved itself (as had been expected) a very effective instrument for fractionation, without being further modified.

It consists essentially of a flask, of any desired capacity within practicable limits, to which a side tube is attached, the latter being held parallel to the neck of the flask, and connected with it, by two smaller tubes at the top and bottom. The upper of these (which serves to carry the outgoing vapor) communicates directly with the upper end of the flask-neck; while the lower tube, which serves to return the prematurely condensed liquid to the flask, is a constricted continuation of the side tube itself, and is bent into a shallow U, fused into the flask-neck a few centimeters above the bulb. The relative positions and sizes of these tubes are shown in the drawing (Fig. 1). The lower connecting U-tube should be very narrow in diameter, and bent in such a way that the orifice at the flask-neck is not much more than the tube's diameter above its lowest point, so as to minimize the amount of dead space which can hold and thereby waste the liquid being distilled.

The vertical side tube is left open at the top, where it is constricted
to such a diameter that it will receive and hold closely the shell of the
Beckmann thermometer at a point near the zero mark.   No cork should
be used; the thermometer may easily be made to fit without grinding
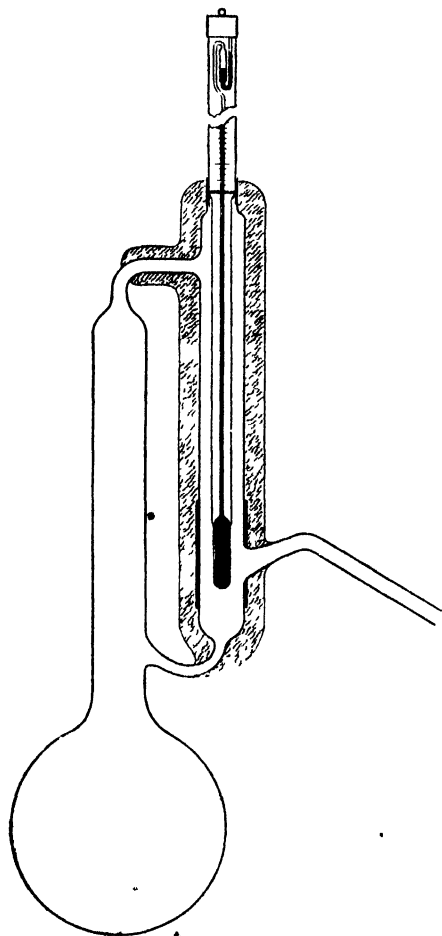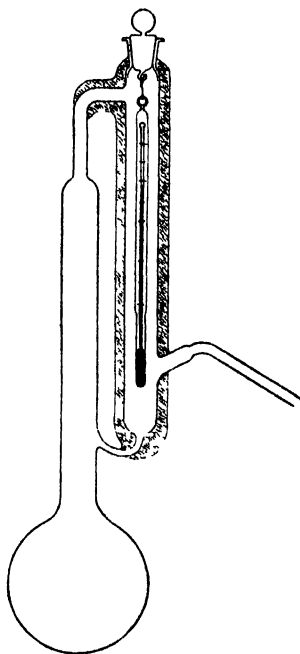
Fig 1.   Fig. 2.

closely enough to prevent the escape of vapor, for a liquid seal will collect
in the annular space at this point.   If necessary, a packing of clean as-
bestos fiber will make the closure secure.   With hygroscopic liquids,
of course, the thermometer must be fitted into place with a ground joint.
The delivery tube should be wide, and should be bent upward at the

point where it leaves the side tube, so as to cause condensed liquid from the bulb of the thermometer, or from the walls, to flow back into the flask, and not into the condenser.   A mirror of tinfoil to prevent radiation may advantageously be bound around the side tube so as to surround the thermometer bulb, and the whole of this tube as well as the upper connecting tube should be encased in a thick shell of asbestos

When liquid is boiled in this apparatus, there is, of course, an almost complete reflux condensation until the tubes reach the temperature of ebullition   In full operation, the distillation should be not rapid, but very steady   All that condenses before the delivery tube is reached returns to the flask through the narrow lower connecting tube, and only that part which still remains as vapor after the long journey passes out into the condenser   No stream of superheated vapor can rise around the thermometer, nor direct spatterings from the liquid impinge upon it   When the tubes are well insulated thermally, the irregular motions imparted to the vapor-stream by the shape of the tubes seem to be sufficient to render the vapor thermally homogeneous when it reaches the thermometer bulb   Here the presence of both vapor and liquid in approximate equilibrium enables the temperature at the moment of egress into the condenser to be accurately determined

The essential feature of the apparatus is the fact that in it the whole uncertain stem of the thermometer, practically up to the zero of the Beckmann scale, is kept really at the temperature of the vapor   The importance of this precaution in determining any exact temperature with the Beckmann thermometer can hardly be overestimated   The degree of uncertainty introduced by a merely partial heating of the lower tube of this instrument may be very great   Moreover, the bulb of the thermometer is exactly opposite the exit tube into the condenser, so that the thermometer indicates the true temperature of the vapor which is actually being condensed, as nearly as possible   In these respects it is very different from the Claisen form.

Another modification of the same type of still is seen in Fig 2   This is intended for use with small Anschütz thermometers, it is like the first modification except for the addition of a hooked glass stopper to the side tube, and the inserting of mica windows into the asbestos shell around this tube   When liquids are to be distilled which leave much insoluble residue, another stopper on the neck of the flask itself facilitates cleaning, but this is not necessary   Electric heating by an immersed platinum coil[1] is practicable, and with non-conducting liquids advantageous   The use of platinum scrap, fragments of porcelain, or the like to introduce the gaseous phase into the body of the liquid is, of course, advisable, but

[1] See Richards and Mathews, *Proc Am Acad*, **43**, 21 (1908), also Beckmann *Z physik Chem*, **64**, 506 (1908)

except in order to prevent violent bumping, such precautions are less necessary than with the simple boiling flask. In our work the flask was usually heated with the naked flame, which gives less trouble from super-heating than a more evenly distributed source of heat of lower temperature.

To prevent irregular cooling from the outside, especially when high boiling liquids were being distilled, the whole still, together with the burner beneath, was enclosed in a cylindrical asbestos box, or air-bath, through which only the outlet tube and the stem of the thermometer protruded. By proper manipulation of the flame, or with the help of a second lamp, the whole system could be kept at a sufficient constant temperature, while through a mica window in the protecting jacket the boiling liquid could be watched.

An example of the progress of a typical case will show the efficiency of the apparatus. Five hundred cubic centimeters of a good commercial toluene were fractionated, six fractions being collected in each distillation and each of these fractions distributed into six others in the following. After six such complete distillations, the final product, 130 cc. in volume, redistilled within an interval of 0.02°, although the original range of boiling point was at least fifty times as great. Two more fractionations of a half of this material yielded 40 cc. of a product which distilled within a range of less than 0.01° under barometric pressure constant during the time of distillation; and very nearly all of this purer material redistilled over the same range. By immediate immersion of the warm,[1] dry bulb of the standardized Beckmann thermometer (which had a range of 20°) into a carefully regulated steam bath, the difference between the two boiling points of toluene and water was thus measured, and the boiling point of the toluene determined to within 0.01°.

Although no claim is made that this sort of still is more efficient than some of the other forms, it is seen to possess advantages with regard to exact thermometry not possessed by any other usual form. Moreover, stills of this type will be found to be not only sufficiently effective in operation (as is evidenced by the data just quoted), but also convenient in use. They are uncomplicated in design, and are, therefore, inexpensive. They are not cumbersome, and are easy to handle. If properly made they are by no means fragile, and will not crack at the joints if they are gradually heated with ordinary precaution, and if no cold liquid is put into them while they are hot. Made of Jena glass, they are very resistant to fracture by irregular heating, made of silica, they can be used at high temperatures still more safely; and they may be used with resistance thermometers if desired. They may easily be cleaned and are much more practicable

[1] The thermometer was allowed to fall just below 100° so that the boiling point of water should be read on a rising thread

than some of the more complicated still heads. Distillations from this apparatus are also accompanied by little loss, because the surface of condensation is small, and the liquid retained by the U-tube may be reduced to a very slight amount by constricting its diameter. But the most important object of the apparatus, as already stated, is the exact determination of the boiling point of the actual distillate.

CAMBRIDGE, MASS,

NEW BOOKS.

Laboratory Experiments in General Chemistry. Designed especially for use with Stoddard's Introduction to General Chemistry 22 pp. Northampton, Mass.: Gazette Printing Co., 1913. Price, 30 cents.

This collection includes 159 experiments, about two-thirds being devoted to the nonmetallic elements. These are followed by a brief treatment of the metals, including simple directions for their identification. The last eight experiments are quantitative. All of the experiments are well selected and the directions to the student are brief, even meagre. Some modification of the order is desirable, but this is easily accomplished since the loose-leaf plan is employed. The collection is well suited for use in the smaller laboratories. B. S. HOPKINS.

Handbuch der Mineralchemie, Vol. II, No. 5 (Bogen 41–53) with Titelbogen. DOELTER, et al. Dresden and Leipzig: Theodor Steinkopff. Price, M. 9.10.

Mineralochemie in the modern sense is only just emerging from mineralogy, and that only at certain points. The mass of our knowledge pertaining to minerals is still practically unchanged in form since a much earlier day. The present volume is peculiarly arid in that it deals with matter which has been practically untouched by modern ideas. There are a few hydrous silicates, the role of water in which has been experimentally studied, and there are some synthetic data on the silicates of copper, lead, and zinc, but they are mostly of a fragmentary sort, made without much regard for physical conditions or chemical relations. A great many pages are devoted to jade and nephrite; there are long tables of analyses and many physical constants, the latter probably determined not infrequently, as was the habit of the earlier physicists, on material of unknown composition; but of mineral chemistry there is practically none. However, the editors should not be blamed for omitting what does not as yet exist.   .   E. T. ALLEN.

Praktikum der Wasseruntersuchung. By PROF. DR. O. EMMERLING. Gebrüder Borntraeger, Berlin, 1914. Price, 7 mk., 20 pfg.

This little book of approximately 200 pages covers the entire field of chemical, biological, microscopical, and bacteriological water examination, in a very clear and concise manner. The "chemical examination" in-

cludes also determinations of electric conductivity, gas analysis and biological oxygen consumption. One chapter is devoted to the examination of mineral water and the determination of the radioactivity. The chapter on the examination of sewages deals with the determinations of oxygen, hydrogen sulfide and iron sulfide, putrescibility, phosphoric acid, organic carbon, the nitrogenous constituents, etc. The most important impurities in trade wastes are thoroughly discussed, and methods for the determination of some of the impurities given. The biological-microscopical part of the book is excellently treated, and represents the latest views of the German school. The Germans have developed this field in a manner hardly appreciated by the majority of the American water and sewage chemists. This part of the book in particular is profusely illustrated. The illustrations are of a high order and are present in sufficient numbers to fulfill the needs of the routine water and sewage chemist. The organisms are divided into three classes, representing the different stages of self-purification. The organisms characteristic of each stage are enumerated. The German method of collection and enumeration of plankton is likewise given. The last chapter deals with the routine bacterial examination of waters and the preparation of media. A short interpretation of the results obtained by the chemical analysis and a discussion of the German laws dealing with the sanitary qualities of the water and the prevention of stream pollution are appended.   ARTHUR LEDERER.

[COMMUNICATION FROM THE MASSACHUSETTS AGRICULTURAL COLLEGE.]
THE ELECTRO-TITRAMETRIC METHOD AND ITS APPLICATION TO GENERAL ANALYTICAL CHEMISTRY.
BY F H HESSELINK VAN SUCHTELEN AND ARAO ITANO
Received June 23, 1914

Since the time of the first use of the empirical normal solutions of Gay-Lussac and the introduction of present normal solution of Ure, volumetric analysis has never received such a strong impulse as that through the application of physical chemistry.   This is especially true for the volumetric determinations of acids and bases, in so far as the nature of neutralization is now clearly understood.   Our knowledge of the role which indicators may play in neutralization has been increased in recent years very markedly by the introduction of the dissociation theory.   We do not consider that this is the place to go into a discussion of indicators, but it will suffice to say here that with the knowledge of the necessary · facts, especially of dissociation constants, we may occasionally predict , whether an indicator is applicable in a special case or not.

In spite of the fact that in recent times the theoretical knowledge of the color indicators has been considerably increased, and here and there practical applications drawn from those principles have been made, there are still, as every analytical chemist knows, many embarrassing and unmanageable difficulties to contend with.

We can only touch upon a few of those difficulties.   For instance, the personal equation which can cause an error of 1 cc. in a 0.01 N solution, and further the difficulty encountered with a liquid which possesses a color that may interfere with the recognition of the indicator, and those

complications which may arise in the case of very dilute solutions. These are only a few of the reasons why the application of indicators in the general analytical field of chemistry is rather limited.   It is therefore not unexpected that attempts have been made to overcome these difficulties by the introduction of another type of indicators which are dependent on and indicative of the physico-chemical changes in the solution.

W. Böttger[1] some years ago, in the case of colored or turbid solutions in which the change of color of an indicator would be more or less masked, recommended the use of the electrometer.   It must be said, however, that determinations with this instrument are more laborious and that such measurements are less familiar to chemists than the determination of conductivity.   It is the merit of Küster[2] and his associates to have shown that such titrations, which cause great difficulty and uncertainty, could be made with a high degree of accuracy if, instead of depending on the change of color, use was made of the change of physical-chemical property (electrical conductivity) of the liquid by the process of neutralization.   We may conclude from their work that the point of neutrality between strong acids and bases can be determined much more exactly by conductivity methods than by the use of indicators.   Also, if weak acids were used, as for example tartaric and acetic acids, which, as is well known, have caused so many difficulties by the ordinary titration method, sharp and good results were obtained by the use of the conductivity method.   The point of neutralization of red wine by means of the conductivity determination was much more definite than if determined by titration with litmus.   The attempt was also made by them to titrate four quinine derivatives by the electro-conductivity method with good success.   Further, Duboux and Dutoit[3] have used this conductivity titration in many of their special researches in wine analysis.   From their interesting work, which treats especially the organic acids in wine, we may say that the conductivity titration has proved here also to be a very successful and helpful aid in chemical analysis.

The preparation of exact ammonium citrate solution, which previously gave rise to difficulties, has been solved by the application of the above mentioned method by Hall and Bell,[4] who showed by this method an exactly neutral solution of ammonium citrate was easily prepared.

In our analysis of soil solutions,[5] we had already used the method of titration by conductivity in determining the acid and basic binding capacity of such solutions.   We feel that it would be superfluous here to go into

[1] W. Böttger, *Z. physik. Chem.*, **24**, 253–301 (1897).

[2] F. W. Küster, M. Grüters, and W. Geibel, *Z. anorg. Chem.*, **42**, 225–34 (1904).

[3] P Dutoit and M. Duboux, *J. suisse de Chim. et pharm.*, **1906**, p. 690.

[4] *J. Ind. Eng. Chem.*, **3**, 559 (1911).

[5] F. H. Hesselink van Suchtelen and A. Itano, *52nd Ann. Rept. Mich. Board of Agr.*, p. 149 (1913).

the fundamental principles underlying this method of analysis, since they may be considered to be the common property of the analytical and biological chemists; and there is no lack of excellent manuals dealing with the practical phases of measurements of electrical conductivity. We will, therefore, confine ourselves to a brief summary of results and call attention to precautions necessary in carrying out our technique.

It must be said that in the execution of such conductivity titrations, certain precautions have to be followed. These will be treated very briefly because such rules can be deduced easily from the theoretical basis of the applied method and from hydrolysis.

It is quite evident that in most of our experiments a determination of the cell constants did not need to be considered, because it was only necessary to have the relative bridge readings. An exception, however, was made in the case of physiological liquids, such as urine and milk, because such determinations of specific conductance may be of special clinical value.

Because of the fact that electrical resistance varies greatly with temperature, greatest care must be taken that the solutions are not subjected to changes of temperature at the time of titration. In our case, the conductivity cup (filled with vertical electrodes) stood deep in a large 75-liter water bath, and throughout the time of titration the cup remained in the liquid. The cup was agitated by gentle shaking in order to facilitate rapid intermixture.

To relieve the operator of the tedium and strain of acute listening through the telephone receiver, we have substituted in many of our experiments, especially where dilute solutions were employed or a high degree of accuracy was required, an alternating current galvanometer which permitted far sharper determinations to be made. The use of such a galvanometer is advisable, but not essential.

To those familiar with this field of work, this short introduction does not claim to disclose any new point of view, nor, for those not so well versed in these subjects in question, do we attempt an exhaustive presentation of the fundamental supporting theory.

We will now proceed to consider the individual curves, and there, as the case may arise, enlarge upon certain features necessary to an understanding of the subject. We deem it advisable to start with the most simple case in our analysis, namely, the titration of acids and bases, because they may be considered as the basis of our work.

In the preceding paragraphs we have discussed some of the typical features and peculiarities of this special conductivity titration. Let us turn now to a comparison of the accuracy of this method with that of a color indicator. We see at once that the values for neutrality, as obtained by

means of phenolphthalein, are all without exception more alkaline than those determined from the conductivity titrations.

The question now arises, "Which method gives the neutral point with greater accuracy?" In deciding this question, use was made of the indicator table so thoroughly worked out by Sörensen. It was easily demonstrated that by the use of an appropriate indicator with a sharp color change at the neutral point, results were obtained which agreed with the conductivity titration. Besides this, it is a well-known fact that the neutral point of phenolphthalein is decidedly alkaline.

It must be noted here that of the above curves, only one (No. 1) was made by an experimenter who was familiar with conductivity titrations. The others were all worked out by men performing the experiment for the first time. This fact leads to an important feature of the conductivity titration; namely, that the influence of the subjective factor which necessarily enters into every chemical analysis is here minimal. This fact will be borne out by a consideration of the above curve.
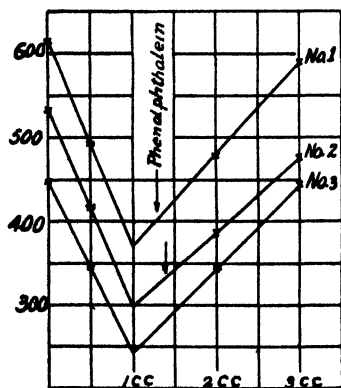
Neutralization of strong acid by strong base.
In cup 10 cc 0 001 N H₂SO₄
Titrated with 0 01 N NaOH

Readings

	No I	No II	No III
0	615 0	533 7	447 5
0 5	492 5	417 6	345 0
2 0	447 5	387 5	342 0
3 0	590 0	477 0	443 0

Theoretically, 0 1 cc
Found, 0 1 cc

Fig 1
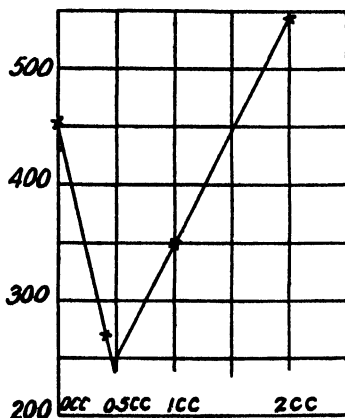
Neutralization of 5 cc 0 001 N H₂SO₄
with 0 01 N NaOH

Readings.

0 cc	457 5
0,4 cc	267 5
1 0 cc	350 0
2 0 cc . .	544 7

Theoretically, 0 5 cc
Found, 0 5 cc

Fig 2.

It should be added that many of these curves were made without the use of a galvanometer. It is evident that the use of this instrument will still further minimize the influence of the personal equation. The significance of this elimination is emphasized, on the contrary, by a glance

at the varying results obtained by different experimenters using phenol-phthalein—an indicator noted for the sharpness of its color change.

As may be seen from the graphs, it is an *a priori* fact in conductivity titrations that they are not characterized, as are the color indicator titrations, by a total dependence on one single point at which the color changes. The conductivity titration, on the contrary, is typified by lines, each line being fixed and determined by a series of points, the number of which is under the control of the experimenter. We consider this to be an important advantage over the color indicator method, for many interesting deductions can be drawn from such curves.

In regard to the point of inflection, we may say that it is sharply defined and determinable with exceeding precision. As an illustration of this, the following graph may serve. In this case o oo1 N 5 cc H_2SO_4 were titrated with o o1 N NaOH. Even in this concentration, the result was satisfactory.

In the following experiment the electro-titrametric method was employed for the titration of a weak acid (lactic acid) with
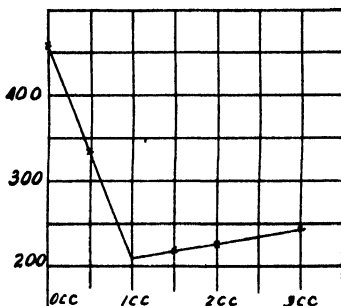
Neutralization of a weak acid (lactic acid) by 0 1 N NaOH
In cup 5 cc 0 1 N NaOH (and phenol-phthalein)
Titrated with 0 5 N C$_3$H$_6$O$_3$

	Readings
0	457 5
0 5	335 5
1 5	220 0
2 0	227 5
3 0	245 0

Theoretically, 1 cc
Found, 1 cc
Turning point phenolphthalein, 1 07

Fig 3
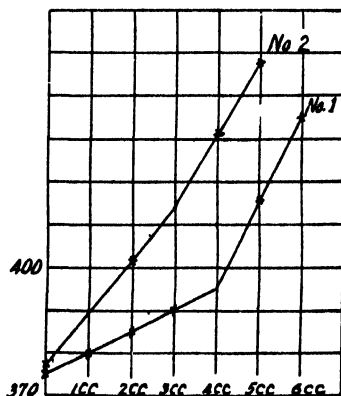
Determination of malic, tartaric and succinic acids

In cup 5 cc 0 1 N tartaric ⎫ and 40 cc 95%
5 cc 0 1 N succinic ⎬ alcohol
10 cc 0 1 N malic ⎭ 0 2 cc 28% NH$_4$OH

Titrated with 0 5 N barium acetate

Readings No 1		Readings No 2	
0 cc	375	0 cc	377 5
1 cc	380	2 cc	401 5
2 cc	385	4 cc	432 9
3 cc	390	5 cc	448 0
5 cc	415	Total	acids—suc-
6 cc	435	cinic	as No 1
Total acids		plus 1 cc	36%
		acetic	acid

Fig 4

a strong base (NaOH)—a titration which had hitherto been attended with many difficulties.

The amount of lactic acid was determined by the formation of its zinc salt, and, in accordance with this, a normal solution was prepared (theoretical inflection point, 1 cc.; found, 1 cc.). Here again, as in the experiments described in the foregoing, the electro-titrametric method proved to be of especial value, because of the high degree of precision with which the neutralization point was obtained. It is to be noted here that the titration in this case was performed in the reverse of the usual manner; i. e., the NaOH was placed in the conductivity cup and the acid was added to it from the buret. The reason for this procedure is at once evident and requires no comment.

The graph (Fig. 4) is an illustration of the determination of various organic acids (malic, tartaric and succinic). It is interesting to note that in the case where no acetic acid was added (No. 1), the result was in perfect accordance with the total amount of acids present. In the determination, however, when an addition of acetic acid had taken place (No. 2) only tartaric acid and malic acid showed their presence.

Up to now, we have considered simply the determination of neutralization points. This naturally is the most ordinary kind of determination to make first, but in no way marks the limitation of the sphere of usefulness of the method. We feel confident that the electro-titrametric method will find a constantly widening field of application, and this will naturally be a source of personal gratification to us, should it prove to be the case. The experiments which we have performed are necessarily limited in number and kind, being confined to the determination of those elements and radicals known to be of particular importance in general and biological chemical analysis.

At this juncture we wish to emphasize two points that strongly commend this method, namely, accuracy and ease of performance. The elements and radicals included in our determinations were, Cl, Ag, SO_4, Ba, U, PO_4, NO_3, K, Ca, Fe''.

In the first determinations of those elements and radicals, we aimed to test the method as to its application and limitations, and we used, therefore, chemicals of highest purity (Kahlbaum), even going so far as to check their purity by standard methods of analysis.

The first of these experiments was a determination of Cl in KCl by means of $AgNO_3$. Fig. 5 shows the sharpness and precision which characterizes the determination. The value obtained by the conductivity titrations coincided exactly with the theoretical value (theoretical, 35.46 mg. Cl; found, 35.46 mg. Cl).

The next analysis was the determination of SO_4 in K_2SO_4. In the cup was 10 cc. $N/10$ K_2SO_4. This was titrated with $N/3$ $Ba(NO_3)_2$.

At this point, attention should be called to the fact that, in order to obtain the highest degree of precision, we introduced, in many instances into the cup, a very small portion of the salts yielding the precipitation to be expected. It will be seen that in addition to what has been said already, the analysis of K_2SO_4 by the electro-titrametric method does away with the laborious processes of precipitation, incineration, and weighing, and avoids the many opportunities for error engendered by these operations.
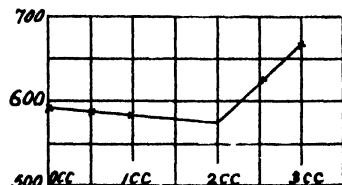
Determination of Cl
In cup 10 cc 0 1 N KCl
Titrated with 0 5 N AgNO₃

	Readings.
0 cc	592
0 5 cc	586 5
0 955 cc	582 3
2 000 cc	576
2 55 cc	629 5
3 00 cc	668 3

Theoretically, 2 cc = 35 46 mg Cl
Found, 2 cc = 35 46 mg Cl
Fig. 5.

Determination of SO₄
In cup 5 cc 0 1 N K₂SO₄
Titrated with $N/3$ Ba(NO₃)₂

	Readings
0 cc	463 0
1 06 cc	452 1
2 005 cc	485 0
2 986 cc	567 8

Theoretically, 1 52 cc $N/3$ Ba(NO₃)₂ = 240 175 mg SO₄
Found, 1 58 cc = 240 175 mg SO₄
Fig. 6

The next determination was that of PO_4 in $(NH_4)_2HPO_4$, the titration being formed with uranium nitrate as reagent. A glance at Fig. 7 shows that the analytical result agrees exactly with the amount introduced.
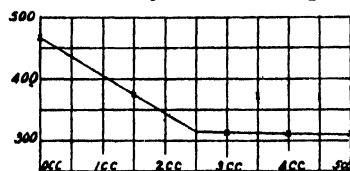
Determination of PO₄
In cup 10 cc 0 1 N (NH₄)₂HPO₄
Titrated with 0 25 N UO₂(CH₃COO)₂

	Readings
0 cc	466 5
1 5 cc	375
3 0 cc	311
4 0 cc	310
5 0 cc	310

Theoretically, 2 5 cc contains 31 68 mg PO₄
Found, 2 5 cc contain 31 68 mg PO₄
Fig 7

Determination of NO₃
In cup 5 cc 0 1 N NaNO₃
Titrated with 0 25 N C₂₀H₁₆N₄ (addition of 1 drop 1 1 H₂SO₄)

	Readings
0 cc	401
1 5 cc	297 5
2 5 cc	257 5
3 5 cc	245 0

Theoretically, 2 cc = 31 005 mg NO₃
Found, 2 cc = 31 005 mg NO₃
Fig. 8

This analysis in particular is noteworthy because of the fact that in using the ordinary indicators (cochineal or potassium ferrocyanide) the turning points are not very definite; and, in general, leave much to be desired.

Another electro-titrametric determination was that of NO_3 in a solution of $NaNO_3$ (a salt which may be looked upon as chemically pure Chili saltpeter), containing also free H_2SO_4. This solution was titrated with a o 25 N solution of nitron in acetic acid. In this experiment, where the theoretical amount of nitrate present was 31 005 mg., the electro-titrametric method again showed perfect coincidence. A differential determination of nitrates and nitrites is possible by the use of hydrazine sulfate.

In the experiments now to be described, determinations were made of several cations. The first was that of K in KCl (Sylvin). The reagent used here was sodium cobalt nitrite. The result obtained was once more in exact accord with the theoretical calculation actually present, 39.10 mg., determined by the conductivity titration, 39 10 mg.
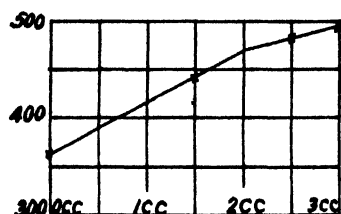
Determination of K
In cup 10 cc 0 1 N KCl
Titrated with 0 5 N Na₃CO(NO₂)₆

	Readings
0 cc.	362 5
1 5 cc	.. 442
2 5 cc	482
3 0 cc	495 5

Theoretically, 2 cc = 39 10 mg K
Found, 2 cc = 39 10 mg K

Fig 9
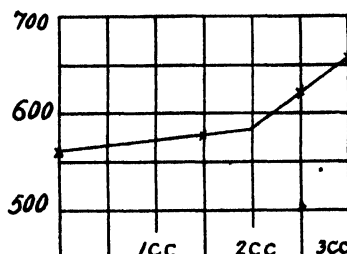
Determination of Ca
In cup 10 cc 0 1 N CaCl₂
Titrated with 0 5 N H₂C₂O₄

	Readings
0 cc	562 5
1 5 cc	578 0
2 5 cc	623 5
3 0 cc.	657 5

Theoretically, 2 cc = 20 035 mg Ca
Found, 2 cc = 20 035 mg Ca

Fig 10

In this case the precipitation requires 3–4 minutes for completion. The conductivity reading then becomes constant. Although the conductivity curve in this instance permits of reasonably high accuracy, it is nevertheless not as sharp as in the other determinations which preceded, or in those which follow it. We have, however, good grounds for the belief that by the use of another cobalt nitrite a sharper graph would result; in any case the reagent must be used fresh.

The next determination of a cation was that of Ca in CaCl₂. The re-

agent used was 0 5 N oxalic acid. As before, the result of the analysis checked with the theoretical amount present.

The next experiment was the determination of the Fe″ content of $FeCl_2$. The titration was performed with 0 5 N Na_2S. One can hardly fail to be struck here with the extraordinary sensitivity of the electro-titrametric method so notably illustrated by the results of this experiment. Thus, 2 792 mg. Fe″ was dissolved in the conductivity cup. A glance at the graph shows that by the analysis exactly this amount was found to be present.

Up to now we have considered exclusively the analysis of elements and radicals in a solution containing only the pure salt. It is hardly necessary to say that by the application of such reliable and specific reagents as we used, the accuracy of the results would not be affected by the presence of foreign substances. Many experiments have convinced us of the applicability of the electro-titrametric method in the case of a solution of a mixture of salts. We invariably found that the presence of salts other than the one in question did not cause variation or inaccuracy of results. For this reason we feel it unnecessary to go any further into this question, resting content with the statement that intelligent choice of the reagents used will,
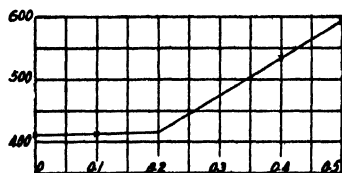
Determination of Fe″
In cup 1 cc 0 1 N FeCl₃
Titrated with 0 5 N Na₂S

	Readings
0 cc	410
0.1 cc	410 7
0 4 cc	535
0 5 cc	594

Theoretically, 0 2 cc = 2 792 mg Fe″
Found, 0 2 cc = 2 792 mg Fe″

Fig 11
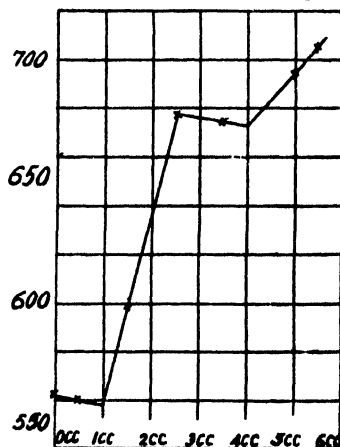
Determination of Cl′ and SO₄ in the same solution
In cup 5 cc 0 1 N NaCl, 5 cc 0 1 N K₂SO₄
Titrated with (A) 0 5 N AgNO₃, (B) $N/3$ Ba(NO₃)₂

A.		B	
Readings			
0 cc	563 0	0 cc	678 0
0 5 cc	560 5	1 0 cc	675.0
1 5 cc	598 5	2 5 cc	694 5
2 5 cc	678 0	3 0 cc	706.0

A
Theoretically, 1 cc = 35 46 mg Cl.
Found, 1 cc = 35 46 mg, Cl

B
Theoretically, 1 51 cc = 96 09 mg SO₄.
Found, 1 5 cc = 96.09 mg SO₄.

Fig. 12.

in the case of a mixture of substances in solution, prevent the possibility of even the slightest disturbance. A single illustration of this may be seen in Fig. 12, representing the determination of four different substances, Ag, Cl, Ba, SO_4, in a solution containing a mixture of K_2SO_4 and NaCl. The graph speaks for itself in language that is unmistakable.

Previously, we dealt with the determination of acids, bases, salts, and
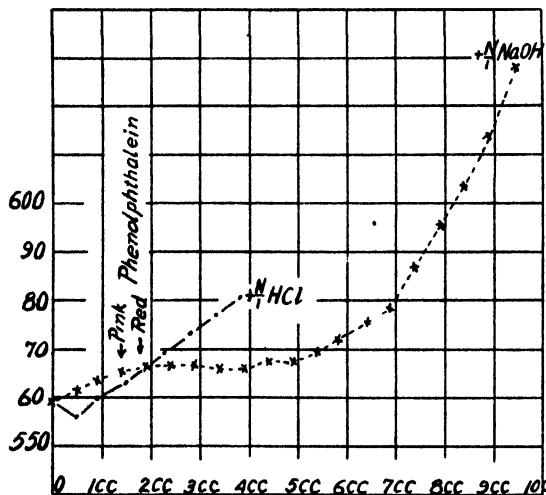
Determination of the acid and basic binding capacity (HCl, NaOH)
of urine (sp cond 260 5¹⁰ ⁴)
In cup 50 cc urine
Titrated with (A) N HCl, (B) N NaOH

Readings Acid binding (A)		Readings Base binding (B)			
0	555 0	0	559 0	4 9	567 5
0 5	556 5	0 5	561 5	5 4	569 5
0 9	560 0	0 9	564 0	5 9	572 0
1 5	563 5	1 4	565 5	6 4	575 5
2 3	569 5	1 9	566 5	6 9	581 0
2 8	573 5	2 4	567 0	7 4	587 0
3 3	577 0	2 9	567 0	7 9	595 5
3 8	580 7	3 4	566 0	8 4	603 5
		3 9	566 0	8 9	614 0
		4 4	567 5	9 4	628 0

Fig 13

mixtures of salts. At this point we take occasion to state that this method, which was so successful for the above mentioned substances, was also of great value in the analysis of liquids of biological constitution. We have purposely concentrated the largest part of our attention upon the analysis of the working basis of the method in its wider applications. Therefore, we reserve, for later publication, the analysis of biological liquids. We may, however, remark that by means of our method of analysis of the

chlorine and phosphate in such liquids (for example, urine) no difficulties were presented, the results being in perfect accord with those obtained by the other methods   The advantages of the electro-titrametric method in these latter instances are, the possibility of an exact analysis of a few cubic centimeters, and at the same time an extremely high degree of precision

It is necessary here to call attention to the fact that in the determination of SO_4 in such liquids certain complications were encountered, which impressed us with the fact that we had to deal with a liquid of different composition from the synthetical solution   Observing certain precautions, as for example, degree of acidity, kind of reagent, etc , we were in some instances able to obtain results which closely agreed with those of gravimetric determinations

The last curve is an illustration of the acid and base binding capacity of a physiological liquid, in this case urine   The previous statement in regard to the use of indicator is especially true in this case   It should not be overlooked, however, that the direction of the curve in such cases is probably not entirely due to the above stated phenomena, because other factors, such as changing viscosity, may affect the total result   It is interesting to note that in this connection successive precipitations were observed after the addition of certain amounts of the reagent

It is the belief of the writers that such curves may prove to be in some cases a more instructive demonstration of the complex properties of such liquids and that more deductions might be drawn from such curves than those from a turning point of an indicator

As the nature of this publication is preliminary, the authors wish to reserve the right to develop this field more completely in the near future

AMHERST MASS

A RAPID LABORATORY METHOD OF MEASURING THE PARTIAL VAPOR PRESSURES OF LIQUID MIXTURES.

BY M A ROSANOFF C W BACON AND R H WHITE [1]
Received July 2 1914

Section I.—Introductory Remarks.

It is scarcely necessary to point out that the partial pressures of volatile mixtures are not measured as such   What is really determined, is the composition of the vapor which is in equilibrium with the liquid mixture The partial pressures are then assumed to be proportional to the molar percentages of the components in the vapor, and their absolute values become known if the total pressures have been determined manometrically

The main difficulty involved is that of analyzing the vapor with sufficient precision. The method that has been most extensively used in the past consists in distilling off a small amount from the given mixture and analyzing the distillate, on the assumption that if the relative amount of distillate is sufficiently small, its composition is very close to that of the first trace of vapor given off by the liquid. As the precision and reliability of this method are in many ways subject to doubt, and as the results obtained have often been found to disagree with those yielded by other methods, it appeared desirable to devise a method, the reliability of whose results should, as far as possible, be free from doubt. Such, we believe, is the method devised by Rosanoff, Lamb, and Breithut,[1] and worked out in its practical details in these laboratories.[2] It consists, briefly, in passing a binary vapor of constant composition through a liquid mixture of the same substances; as long as the liquid is not in equilibrium with the vapor, its composition changes, and consequently both its boiling point and the vapor escaping from it change continuously. When the composition of the liquid has finally adjusted itself to that of the vapor employed, and equilibrium has set in, everything becomes constant: the thermometer in the liquid indicates a constant temperature; the escaping vapor has ceased changing, and consecutive fractions of it condensed show the same composition. The attainment of equilibrium is thus attested in two independent ways, and as the condensed fractions can be taken as large as desired, the analytical difficulties disappear, and the composition of the equilibrium vapor becomes known with all precision necessary. Unfortunately, the required apparatus is somewhat complex, and its efficient handling calls for considerable manipulative skill, so that the method can scarcely be recommended for ordinary use, in connection with studies of either the theory of solutions or fractional distillation.

The method just referred to has served to demonstrate that reliable partial pressure data can be obtained by distilling off a small fraction, as has long been practised. Thus, the well-known results obtained by v. Zawidzki[3] are doubtless very good. Only, on account of the tendency of certain impurities, such as moisture, to accumulate in the first distillate, the organic liquids employed must be exquisitely purified, and the small distillate to be analyzed must be handled with great care, if its composition is not to be grossly affected by evaporation. Furthermore, even v. Zawidzki's apparatus is of somewhat complex construction and calls for no little delicacy of manipulation. Thus a need still remained for a simpler and more rapid, yet sufficiently reliable, laboratory method.

[1] Rosanoff, Lamb, and Breithut, THIS JOURNAL, 31, 448 (1909); Z. physik. Chem., 66, 349 (1909).

[2] Rosanoff and Easley, THIS JOURNAL, 31, 953 (1909); Z. physik. Chem., 68, 641 (1910).

[3] Von Zawidzki, Z. physik. Chem., 35, 129 (1900).

Such a method is described in the present communication. It was first devised and successfully employed in these laboratories during the year 1910–1911, and a brief preliminary account of it was published in 1911.[1] Since then, however, it has been used here in a number of new cases of both binary *and ternary* mixtures, and to-day we feel justified in recommending it as the easiest method for ascertaining the composition of vapors in equilibrium with all sorts of liquid mixtures. We believe, further, that it would be especially useful where the available amount of substance is too small for the older methods to yield accurate results.

Section II.—Principle of the Method.

The problem is to ascertain the composition of the first infinitesimal amount of vapor given off by a liquid mixture of known composition. To this end we subject the given mixture to distillation, carefully avoiding reflux condensation. The amount finally driven over may be as great as 80 or 90% of the total original weight. And imagine that we have obtained knowledge of what the composition of the distillate was when its weight was, say, 1 g.; what the composition of the distillate was when its weight had reached 2 g., then 3 g., 4 g., 5 g., etc. If the composition of the distillates were now plotted against their weights, a curve would be obtained, every point of which would indicate the composition that the distillate would have when its weight has attained any definite amount within the range of the curve. But only a moderate extrapolation backward would lead up to the composition axis, that is, to where the weight of distillate is zero. The point of intersection would obviously indicate *the composition of the first indefinitely small amount of distillate*, and thus our problem would be solved.

This is, in fact, our procedure. Only, instead of allowing the distillate to accumulate in the receiver, we remove seven or eight consecutive fractions of it, and weigh and analyze them separately. Knowing the weights and compositions of Fractions 1 and 2, we can readily calculate the weight and composition that would have been found if they had been allowed to form a single combined fraction. Similarly, knowing the weights and compositions of 1, 2 and 3, we can easily calculate what the weight and composition would have been if these three distillates had been allowed to form a single fraction, and so forth for the rest of the distillates obtained.

The extrapolation just mentioned indicates, as stated, the composition of the first infinitesimal amount of vapor evolved by the given liquid mixture. But the same experiment yields also further information. Suppose that eight distillates have been collected and that the composition of the residue had been found by analysis. Knowing, again, the weights and compositions of Fractions 8 and 7, we can calculate the weight

[1] Rosanoff, *J. Franklin Inst.*, **172**, 527 (1911).

and composition that would result if the two were mixed, or if they had been allowed to form a single fraction. Similarly, we can find the combined weight and composition of Nos. 8, 7, and 6, then of Nos. 8, 7, 6, and 5, etc. Suppose now that the weight of No. 8 is entered as an abscissa and the composition of No. 8 as the corresponding ordinate; that the combined weight of Nos. 8 and 7 is taken as a second abscissa, and their combined composition as a second ordinate, etc. A new curve would thus result, and this curve again we would extrapolate to intersection with the composition axis. The point on the curve corresponding to distillate No. 8 may be thought of as the composition of the mixture *returned* to the residue when the weight returned, as if by a reversal of the actual distillation, is that of No. 8. Similarly, the point of intersection on the composition axis would represent *the composition of the first infinitesimal amount returned to the residue*. But this is evidently nothing else than the composition of the slight amount of vapor still in contact with the residue. In this manner our one actual distillation teaches, not only what vapor is in equilibrium with the original mixture, but also what vapor is in equilibrium with the final residue. It would be easy to show that simple enough calculation could further reveal the composition of the vapors in equilibrium with mixtures intermediate between the original and the residue. But we will not insist on this point, as we have not made use of it in our practical work.

Section III.—Apparatus and Manipulation.

In applying experimentally the simple principle just stated, an apparatus was devised in which reflux condensation is practically impossible. The apparatus, drawn to scale in cross section, is shown in Fig. 1. It consists of a pear-shaped vessel with a long neck, near the upper end of which are four circular openings for the escape of the vapor. A glass jacket, fused on to the rim of the neck, surrounds the flask and ends below in a tube through which the vapors escape into a powerful worm condenser, and thence, in liquid form, into a receiver having several compartments for the convenient collection of consecutive fractions. The receiver communicates with· the atmosphere through a tube filled with calcium chloride, to keep out moisture. The neck of the pear-shaped boiling-vessel is permanently stoppered above with a cork, which is made thoroughly vapor- and liquid-tight with shellac and sealing-wax. The cork carries an electric heater of platinum wire, and, for the introduction and withdrawal of liquid, an adapter-tube reaching nearly to the bottom of the boiling-vessel. Liquid is introduced and withdrawn with the aid of a separatóry-funnel fitted by means of a tight cork into the upper part of the adapter-tube, as shown in the diagram. During operation the boiling-vessel is thus surrounded by the vapor of the boiling liquid itself, and thus reflux condensation is prevented. But to make doubly sure

of this, the jacketed distillation vessel is all but completely immersed in a bath, whose temperature, roughly constant, is somewhat above the highest temperature that may be attained by the boiling mixture experimented upon.

The manipulation is very simple. A mixture of known composition is introduced into the distilling vessel and is set boiling by means of the electric heater. There being no reflux, the distillation is usually very rapid, each fraction taking only a minute or two to collect. The fractions are received in small, carefully weighed glass-stoppered bottles, and in scarcely half an hour, during which the apparatus requires little attention, the run is complete. Now a sample of the residue is withdrawn for analysis, the several distillates are weighed (with a precision of about 0.05 g.), and finally the residue and the distillates are analyzed as stated above.

We have not mentioned the dimensions of the distillation apparatus. In our earlier work the pear-shaped boiler had a capacity of about 300 cc. and was almost filled with the liquid mixture for a run. To prevent the protrusion of the platinum heater above the liquid, the distillation was usually interrupted when about 100 cc. of liquid still remained in the vessel. More recently a smaller apparatus has been employed here, the pear-shaped boiler having a capacity of only 125 cc., and the shape

Fig. 1.

of the platinum heater was modified to permit of leaving a residue of barely 25 cc. There is, however, no reason why a still smaller apparatus should not be employed when only a scanty amount of experimental material is available.
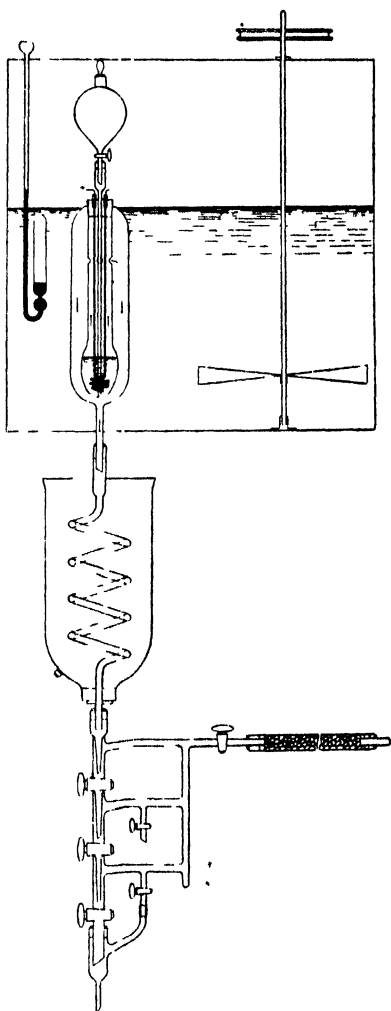
Section IV.—Analytical Method.

The composition of our binary mixtures was determined on the basis of their refractive indices by an interpolation method first recommended by Ostwald and since used by von Zawidzki and also in this laboratory. The indices of a number of mixtures of exactly known composition are determined, and from these the percentages are calculated which would correspond to these indices if the latter obeyed the rule of additivity. The differences between the true and these "ideal" percentages are plotted as ordinates against the ideal percentages themselves. The resulting curve gives the correction to be algebraically added to the ideal percentage, the latter being calculated in any given case from the equation:

$$\text{Ideal percentage} = \frac{100(i - i_2)}{i_1 - i_2}$$

where i_1 is the refractive index of the isolated component whose ideal percentage in the mixture is sought, i_2 is the index of the second component in the isolated state, and i is the observed index of the mixture.

Tables I–III give the corrections for a number of ideal percentages in the case of three pairs of liquids; the data of Tables I and II are based on new measurements; the data of Table III are calculated from the measurements of von Zawidzki.[1] Corrections for other percentages than those given in the tables will readily be found by graphic interpolation. All these corrections lead to the true composition of the mixtures expressed in *molar percentages*.

TABLE I.		TABLE II.		TABLE III.	
CHLOROFORM—TOLUENE.		ACETONE—TOLUENE.		ETHYL IODIDE—ETHYL ACETATE.	

The index of $CHCl_3$ is 1.44301. That of $C_6H_5CH_3$ is 1.49323. Temp. 25.4°. | | The index of $(CH_3)_2CO$ is 1.35662. That of $C_6H_5CH_3$ is 1.49337. Temp. 25.0°. | | The index of the iodide is 1.51009. That of the acetate is 1.37012. Temp. 25.2°. | |

Ideal % $CHCl_3$.	Correction.	Ideal % $(CH_3)_2CO$.	Correction.	Ideal % C_2H_5I.	Correction.
0	0	0	0	0	0
10	+2.04	10	+3.03	10	+4.12
20	+3.72	20	+3.56	20	+6.96
30	+4.72	30	+7.35	30	+8.68
40	+5.26	40	+8.56	40	+9.41
50	+5.32	50	+9.16	50	+9.42
60	+5.04	60	+9.12	60	+8.70
70	+4.43	70	+8.31	70	+6.21
80	+3.31	80	+6.52	80	+5.36
90	+1.68	90	+3.56	90	+2.96
100	0	100	0	100	0

[1] Von Zawidzki, *Loc. cit.*, p. 145.

Tables for the analysis of mixtures of carbon disulphide and carbon tetrachloride may be found in a former communication.[1]

Ternary mixtures, whose partial pressures were determined by the present method, have been analyzed according to the procedure described by Schulze.[2]

Section V.—Purification of the Substances.

Our substances were purified as follows: *Carbon disulfide* was thoroughly shaken with lime, allowed to stand for some time in contact with mercury, dried with calcium chloride, and distilled; a large middle fraction collected for use passed over within less than 0.1°. Kahlbaum's *carbon tetrachloride* required no further treatment than drying with calcium chloride and redistilling, the fraction collected for use boiling again within 0.1°. *Chloroform* from a well-known American manufacturer was washed with dilute sulfuric acid, then with caustic potash, and next, five times with water. After drying with calcium chloride, it was distilled in dim light, a large middle fraction, boiling between 60.9° and 61.0°, being kept for use. A high-grade commercial *toluene* was thoroughly washed with water, dried with calcium chloride, and distilled, the utilized fraction passing over between 109.5° and 109.6°. A quantity of commercial *acetone* was boiled for ten hours with an excess of solid potassium permanganate, distilled off, dried with potassium carbonate. and redistilled; the fraction kept for use passed over within 0.1°. The *ethyl iodide* was prepared by ourselves, from resublimed iodine, absolute alcohol, and pure red phosphorus; the crude product was washed with a solution of caustic potash and with water, then dried with calcium chloride, distilled, and preserved in contact with finely divided ("molecular") silver; the preparation distilled over completely between 72.6° and 72.8°. Finally, a good grade of commercial *ethyl acetate* was washed with a 50% solution of calcium chloride, then dried with fused calcium chloride, and distilled, the utilized fraction passing over between 76.6° and 76.7°.

Section VI.—Results for Carbon Disulfide—Carbon Tetrachloride.

TABLE IV.—RUN A.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % of CS₄.
1....	16.48	1.53177	59.35
2.........	19.43	1.53108	58.96
3........	15.86	1.52815	57.21
4........................	16.00	1.52491	55 25
5........................	23.75	1.52088	52.73
6........................	17.80	1.51639	49.85
7........................	25.23	1.51181	46.79

It would have been advantageous to express the composition of the dis-

[1] Rosanoff and Easley, *Loc. cit.*, p. 970.
[2] Schulze, THIS JOURNAL, **36**, 498 (1914).

tiallates, *not in molar, but in weight percentages*, as the former complicate the calculations unnecessarily. We will, however, reproduce all results in this paper in the form in which they were originally obtained and used.

From the figures of Table IV, calculation gives the following

TABLE V

Distillates combined	Combined weight Grams	Combined composition (Molar % CS₂)	Distillates combined	Combined weight Grams	Combined composition (Molar % CS₂)
No. 1	16 48	59 35	No 7	25 23	46 79
Nos 1+2	35 91	59 11	Nos 7+6	43 03	48 07
Nos 1+2+3	51 77	58 55	Nos 7+6+5	66 78	49 76
Nos 1+2+3+4	67 77	57 79	Nos 7+6+5+4	82 78	50 86
Nos 1+2+3+4+5	91 52	56 51	Nos 7+6+5+4+3	98 64	51 92
Nos 1+2+3+4+5+6	109 32	55 47	Nos 7+6+5+4+3+2	118 07	53 10
Nos 1+2+3+4+5+6+7	134 55	53 92	Nos 7+6+5+4+3+2+1	134 55	53 92

The original mixture (refractive index = 1 49780) contained 36 77 molar per cent CS_2. The third column of Table V shows, by graphic extrapolation, that the vapor in equilibrium with the original mixture contained 60.35 molar per cent CS_2.
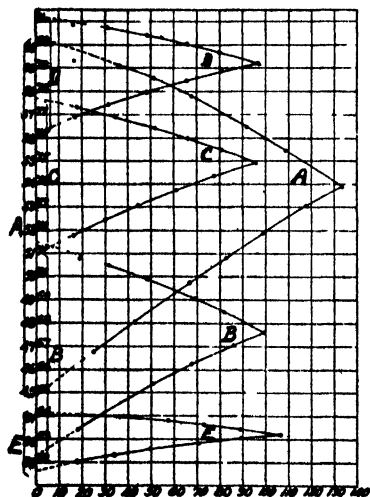
Fig 2.—Carbon disulphide—carbon tetrachloride

The residue (refractive index = 1 48000) contained 22 18 molar per cent CS_2 The sixth column of Table V shows, by graphic extrapolation, that the vapor in equilibrium with the residue contained 44 85 molar per cent CS_2.

The results of Table V are shown graphically by the pair of curves marked *A* in Fig. 2. The curves, it will be seen, are very smooth, and the slight extrapolation introduces practically no uncertainty. Only the first point on the upper curve, corresponding to the first distillate, fails to agree with the rest. The cause of this was doubtless a trace of moisture contained in the original mixture, and if one distillate only had been examined, as is done in the older procedures, an error of at least 1% would have been introduced, probably more. On the other hand, the shape of our curve and its extrapolation are scarcely rendered less certain by the irregularity of that one point.

TABLE VI.—RUN B.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % of CS₂.
1	13.67	1.55285	70.78
2	18.01	1.55168	70.19
3	16.22	1.54901	68.80
4	21.43	1.54582	67.14
5	12.14	1.54200	65.08
6	17.76	1.53890	63.43

TABLE VII.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CS₂.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CS₂.)
No. 1	13.67	70.78	No. 6	17.76	63.43
Nos. 1+2	31.68	70 44	Nos. 6+5	29.90	64.10
Nos. 1+2+3	49.90	69.89	Nos. 6+5+4	51.33	65.39
Nos. 1+2+3+4	69.33	69.05	Nos. 6+5+4+3	67.55	66.22
Nos. 1+2+3+4+5	81.47	68.48	Nos. 6+5+4+3+2	85.56	67.08
Nos 1+2+3+4+5+6	99.23	67.60	Nos. 6+5+4+3+2+1	99.23	67.60

Original mixture (refractive index = 1.51680)	50.11% CS₂
Corresponding vapor (by extrapolation)	71.50% CS₂
Residue (refractive index = 1.49889)	37.62% CS₂
Corresponding vapor (by extrapolation)	62.30% CS₂

The results of Table VII are shown graphically by the pair oı curves *B* in Fig. 2.

TABLE VIII.—RUN C.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % of CS₂.
1	18.25	1.56573	77.28
2	16.80	1.56465	76.57
3	16.66	1.56219·	75.37
4	14.37	1.56002	74 33
5	14.50	1.55767	73.20
6	15.54	1.55486	71 81

TABLE IX.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CS₂)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CS₂.)
No. 1	18.25	77.28	No. 6	15.54	71.81
Nos. 1+2	35.05	76.94	Nos. 6+5	30.04	72.48
Nos. 1+2+3	51.71	76.44	Nos. 6+5+4	44.41	73.09
Nos. 1+2+3+4	66.08	75.99	Nos. 6+5+4+3	61.07	73.72
Nos. 1+2+3+4+5	80.58	75.49	Nos. 6+5+4+3+2	77.87	74.34
Nos. 1+2+3+4+5+6	96.12	74.91	Nos. 6+5+4+3+2+1	96.12	74 91

Original mixture (refractive index = 1.53056)	58 66% CS₂
Corresponding vapor (by extrapolation)	77.70% CS₂
Residue (refractive index = 1.51440)	48.52% CS₂
Corresponding vapor (by extrapolation)	70.90% CS₂

The results of Table IX are shown graphically by the pair of curves *C* in Fig. 2.

TABLE X —RUN D

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of CS_2
1	15 94	1 57393	80 88
2	15 02	1 57336	80 62
3	17 54 ·	1 57171	79 86
4	16 86	1 56966	78 93
5	14 66	1 56771	78 02
6	16 87	1 56534	76 88

TABLE XI

Distillates combined	Combined weight. Grams	Combined composition (Molar % CS_2)	Distillates combined	Combined weight Grams	Combined composition (Molar % CS_2)
No 1	15 94	80 88	No 6	16 87	76 88
Nos 1+2	30 96	80 73	Nos 6+5	31 53	77 42
Nos 1+2+3	48 50	80 43	Nos 6+5+4	48 39	77 96
Nos 1+2+3+4	65 36	80 05	Nos 6+5+4+3	65 93	78 46
Nos 1+2+3+4+5	80 02	79 68	Nos 6+5+4+3+2	80 95	78 87
Nos 1+2+3+4+5+6	96 89	79 20	Nos 6+5+4+3+2+1	96 89	79 20

Original mixture (refractive index = 1 54167)	64 94% CS_2
Corresponding vapor (by extrapolation)	81 22% CS_2
Residue (refractive index = 1 52583)	55 82% CS_2
Corresponding vapor (by extrapolation)	76 13% CS_2

The results of Table XI are shown graphically by the pair of curves D in Fig 2

TABLE XII —RUN E

No of distillate	Weight of distillate, Grams	Index of refraction	Molar % of CS_2
1	18 09	59875	91 00
2	18 28	59848	90 88
3	21 23	59751	90 51
4	15 70	59634	90 06
5	15 78	59520	89 60
6	17 78	59370	89 02

TABLE XIII.

Distillates combined	Combined weight. Grams	Combined composition (Molar % CS_2)	Distillates combined	Combined weight. Grams	Combined composition (Molar % CS_2)
No 1	18 09	92 70	No 6	17 78	89 02
Nos 1+2	36 37	90 94	Nos 6+5	33 56	89 29
Nos 1+2+3	57 60	90 78	Nos 6+5+4	49 35	89 54
Nos 1+2+3+4	73 39	90 63	Nos 6+5+4+3	70 58	89 83
Nos 1+2+3+4+5	89 17	90 45	Nos 6+5+4+3+2	88 86	90 04
Nos 1+2+3+4+5+6	106 95	90 21	Nos 6+5+4+3+2+1	106 95	90 21

Original mixture (refractive index = 1 57895)	83 04% CS_2
Corresponding vapor (by extrapolation)	91 31% CS_2
Residue (refractive index = 1 56701)	77 69% CS_2
Corresponding vapor (by extrapolation)	88 63% CS_2

The results of Table XIII are shown graphically by the pair of curves E in Fig 2. The relation between the composition of liquid and vapor is, on the basis of all the data given in this section, exhibited by the curves of Fig. 3. Here the lower curve indicates the boiling points of the various
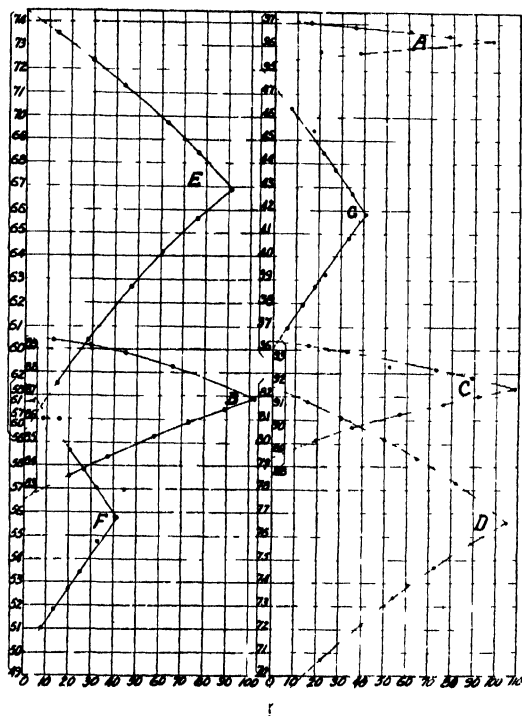
Fig 3.

mixtures. Any horizontal line through the two curves will indicate the composition of a vapor (point of intersection with the upper curve) and of the liquid (point of intersection with the lower curve) in equilibrium with it.

The case of carbon disulfide—carbon tetrachloride was experimentally a somewhat difficult one, owing to the two liquids interdiffusing rather slowly. Nevertheless, the results obtained by the present method are in satisfactory agreement with those yielded by the standard method mentioned above.[1]

[1] Rosanoff and Easley, *Loc. cit*, p 984

Section VII.—Results for Chloroform—Toluene.

TABLE XIV —RUN A

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of CHCl₃
1	16 37	1 44482	97 00
2	20 32	1 44503	96 68
3	24 32	1 44532	96 18
4	17 07	1 44552	95 84
5	20 51	1 44562	95 68

TABLE XV

Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)	Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)
No 1	16 37	97 00	No 5	20 51	95 68
Nos 1+2	36 69	96 82	Nos 5+4	37 58	95 62
Nos 1+2+3	61 01	96 57	Nos 5+4+3	61 90	95 92
Nos 1+2+3+4	78 08	96 41	Nos 5+4+3+2	82 22	96 11
Nos 1+2+3+4+5	98 59	96 26	Nos 5+4+3+2+1	98 59	96 26

Original mixture (refractive index = 1 45153)   85 88% CHCl₃
Corresponding vapor (by extrapolation)   97 25% CHCl₃
Residue (refractive index = 1 45523)   79 54% CHCl₃
Corresponding vapor (by extrapolation)   95 40% CHCl₃
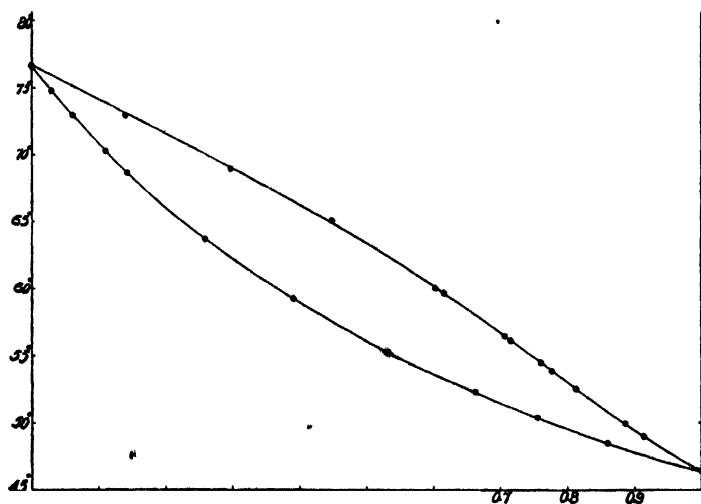
Fig 4.—Carbon disulphide—carbon tetrachloride

The results of Table XV are shown graphically by the pair of curves A in Fig. 4.

TABLE XVI —RUN B

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of CHCl₃
1	13 24	1 44945	89 36
2	15 86	1 44958	89 12
3	15 80	1 45013	88 21
4	20 88	1 45098	86 79
5	17 06	1 45183	85 38
6	20 05	1 45293	83 53

TABLE XVII

Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)	Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)
No 1	13 24	89 36	No 6	0 05	83 53
Nos 1+2	29 10	89 23	Nos 6+5	37 11	84 37
Nos 1+2+3	44 90	88 87	Nos 6+5+4	57 99	85 24
Nos 1+2+3+4	65 78	88 21	Nos 6+5+4+3	3 9	85 88
Nos 1+2+3+4+5	82 84	88 87	Nos 6+5+4+3+2	82 65	86 45
Nos 1+2+3+4+5+6	102 89	86 82	Nos 6+5+4+3+2+1	102 89	86 82

Original mixture (refractive index = 1 46295)   65 33 % CHCl₃
Corresponding vapor (by extrapolation)   89 53% CHCl₃
Residue (refractive index = 1 47015)   51 30% CHCl₃
Corresponding vapor (by extrapolation)   82 55% CH

The results of Table XVII are shown graphically by the pair of curves *B* in Fig 4

TABLE XVIII —RUN C

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of CHCl₃
1	16 74	1 44712	93 20
2	16 11	1 44743	92 68
3	18 69	1 44783	92 01
4	20 98	1 44833	91 19
5	16 81	1 44883	90 36
6	19 51	1 44958	89 12

TABLE XIX

Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)	Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)
No 1	16 74	93 20	No 6	19 51	89 12
Nos 1+2	32 85	92 95	Nos 6+5	36 32	89 69
Nos 1+2+3	51 54	92 23	Nos 6+5+4	57 30	90 24
Nos 1+2+3+4	72 52	92 19	Nos 6+5+4+3	75 99	90 67
Nos 1+2+3+4+5	89 33	91 85	Nos 6+5+4+3+2	92 10	91 02
Nos 1+2+3+4+5+6	108 84	91 36	Nos 6+5+4+3+2+1	108 84	91 36

Original mixture (refractive index = 1 45843)   73 77% CHCl₃
Corresponding vapor (by extrapolation)   93 38% CHCl₃
Residue (refractive index = 1 46490)   61 59% CHCl₃
Corresponding vapor (by extrapolation)   88 20% CHCl₃

The results of Table XIX are shown graphically by the pair of curves C in Fig. 4.

TABLE XX.—RUN D.

No. of	Weight of distillate. Grams.	Index of refraction.	Molar % of CHCl₃.
1	15.19	1.45393	81.80
2	16.74	1.45473	80.40
3	18.05	1.45563	78.83
4	14.75	1.45693	76.50
5	17.31	1.45818	74.23
6	22.70	1.46012	70.65

TABLE XXI.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CHCl₃.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CHCl₃.)
No. 1	15.19	81.80	No. 6	22.70	70.65
Nos. 1+2	31.93	81.06	Nos. 6+5	40.01	73.19
Nos. 1+2+3	49.98	80.25	Nos. 6+5+4	54.76	73.34
Nos. 1+2+3+4	64.73	79.39	Nos. 6+5+4+3	72.81	74.69
Nos. 1+2+3+4+5	82.04	78.29	Nos. 6+5+4+3+2	89.55	75.75
Nos. 1+2+3+4+5+6	104.74	76.61	Nos. 6+5+4+3+2+1	104.74	76.61

Original mixture (refractive index = 1.46956) .... 52.47% CHCl₃
Corresponding vapor (by extrapolation) .... 82.60% CHCl₃
Residue (refractive index = 1.47820) .... 34.64% CHCl₃
Corresponding vapor (by extrapolation) .... 68.59% CHCl₃

The results of Table XXI are shown graphically by the pair of curves D in Fig. 4.

TABLE XXII.—RUN E.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	(Molar % of CHCl₃.)
1	14.47	1.45853	73.60
2	15.49	1.45982	71.21
3	14.02	1.46091	69.18
4	19.31	1.46255	66.09
5	13.44	1.46450	62.37
6	14.55	1.46649	58.50

TABLE XXIII.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CHCl₃.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % CHCl₃.)
No. 1	14.47	73.54	No. 6	14.55	58.50
Nos. 1+2	29.96	72.33	Nos. 6+5	27.99	60.35
Nos. 1+2+3	43.98	71.32	Nos. 6+5+4	47.30	62.68
Nos. 1+2+3+4	63.29	69.71	Nos. 6+5+4+3	61.32	64.14
Nos. 1+2+3+4+5	76 73	68.41	Nos. 6+5+4+3+2	76.81	65.55
Nos. 1+2+3+4+5+6	91.28	66.81	Nos. 6+5+4+3+2+1	91.28	66.81

Original mixture (refractive index = 1.47442) .... 42.61% CHCl₃
Corresponding vapor (by extrapolation) .... 74.80% CHCl₃
Residue (refractive index = 1.48215) .... 26.02% CHCl₃
Corresponding vapor (by extrapolation) .... 56.52% CHCl₃

The results of Table XXIII are shown graphically by the pair of curves *E* in Fig 4

TABLE XXIV —RUN F

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of CHCl₃
1	8 05	1 46559	60 26
2	7 41	1 46589	59 68
3	5 82	1 46813	55 31
4	6 04	1 46837	54 83
5	5 38	1 46926	53 06
6	7 93	1 47030	51 00

TABLE XXV.

Distillates combined	Combined weight Grams	Combined composition (Molar % CHCl₃)
No 1	8 05	59 97
Nos 1+2	15 46	59 98
Nos 1+2+3	21 28	58 70
Nos 1+2+3+4	27 32	57 84
Nos 1+2+3+4+5	32 70	57 04
Nos 1+2+3+4+5+6	40 63	55 83

Original mixture (refractive index = 1 48074)   29 13% CHCl₃
Corresponding vapor (by extrapolation)   61 47% CHCl₃

The residue in this case could not be analyzed.

The results of Table XXV are shown graphically by the upper curve of pair *F* in Fig. 4

TABLE XXVI —RUN G

No of distillate.	Weight of distillate Grams	Index of refraction.	Molar % of CHCl₃
1	7 98	1 47261	46 34
2	9 75	1 47344	44 65
3	4 87	1 47526	40 86
4	5 62	1 47535	40 68
5	6 79	1 47624	38 81
6	6 48	1 47712	36 95

TABLE XXVII.

Distillates combined	Combined weight Grams	Combined composition. (Molar % CHCl₃.)
No 1	7 98	46 34
Nos 1+2	17 73	45 41
Nos 1+2+3	22 60	44 42
Nos 1+2+3+4	28 22	43 67
Nos 1+2+3+4+5	35 01	42 72
Nos 1+2+3+4+5+6	41 49	41 80

Original mixture (refractive index = 1 48483)   19 99% CHCl₃
Corresponding vapor (by extrapolation)   47 23% CHCl₃

The residue in this case could not be analyzed.

The results of Table XXVII are shown graphically by the upper curve of pair G in Fig 4.

The results of all our measurements in the case of chloroform—toluene are exhibited by the curves of Fig 5.
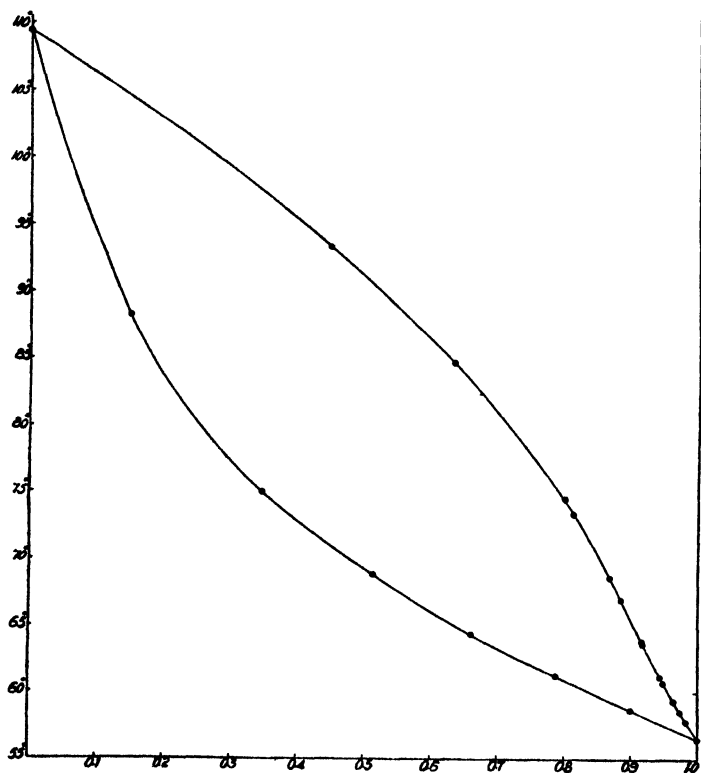
Fig 5 —Acetone—toluene

Section VIII.—Results for Acetone—Toluene.

TABLE XXVIII —Run A

No. of distillate	Weight of distillate Grams	Index of refraction	Molar % of acetone
I	10 42	1 36086	98 10
2	12 57	1 36104	98 01
3	9 61	1 36130	97 89
4	10 12	1 36148	97 82
5	11 48	1 36175	97 72
6	11 29	1 36219	97 52

TABLE XXIX

Distillates combined	Combined weight Grams	Combined composition (Molar % acetone)	Distillates combined	Combined weight Grams	Combined composition (Molar % acetone)
No 1	10 42	98 10	No 6	11 29	97 52
Nos 1+2	22 99	98 05	Nos 6+5	22 77	97 62
Nos 1+2+3	32 60	98 00	Nos 6+5+4	32 89	97 68
Nos 1+2+3+4	42 72	97 96	Nos 6+5+4+3	42 50	97 73
Nos 1+2+3+4+5	54 20	97 91	Nos 6+5+4+3+2	55 07	97 79
Nos 1+2+3+4+5+6	65 49	97 84	Nos 6+5+4+3+2+1	65 49	97 84

Original mixture (refractive index = 1 37023)   93 82% acetone
Corresponding vapor (by extrapolation)   98 10% acetone
Residue (refractive index = 1 37640)   90 67% acetone
Corresponding vapor (by extrapolation)   97 40% acetone

TABLE XXX —RUN B

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of acetone
1	9 19	1 36487	96 27
2	9 43	1 36505	96 22
3	11 42	1 36532	96 08
4	11 83	1 36600	95 76
5	9 42	1 36677	95 4-
6	10 63	1 36727	95 19

TABLE XXXI

Distillates combined	Combined weight Grams	Combined composition (Molar % acetone)	Distillates combined	Combined weight Grams	Combined composition (Molar % acetone)
No 1	9 19	96 27	No 6	10 63	95 19
Nos 1+2	18 62	96 25	Nos 6+5	20 05	95 29
Nos 1+2+3	30 04	96 18	Nos 6+5+4	31 88	95 50
Nos 1+2+3+4	41 87	96 08	Nos 6+5+4+3	43 30	95 63
Nos 1+2+3+4+5	51 29	95 94	Nos 6+5+4+3+2	52 73	95 74
Nos 1+2+3+4+5+6	61 92	95 82	Nos 6+5+4+3+2+1	61 92	95 82

Original mixture (refractive index = 1 38294)   87 11% acetone
Corresponding vapor (by extrapolation)   96 35% acetone
Residue (refractive index = 1 39361)   80 79% acetone
Corresponding vapor (by extrapolation)   94 90% acetone

TABLE XXXII —RUN C

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of acetone
1	8 62	1 36968	94 07
2	12 68	1 36986	93 99
3	11 58	1 37050	93 66
4	13 45	1 37160	93 13
5	9 53	1 37252	92 65
6	10 22	1 37354	92 14

TABLE XXXIII.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)
No. 1	8.62	94.07	No. 6....................	10.22	92.14
Nos. 1+2.................	21.30	94.02	Nos. 6+5............;....	19.75	92.37
Nos. 1+2+3..............	32.88	93.90	Nos. 6+5+4..............	33.20	92.69
Nos. 1+2+3+4..........	46.33	93.73	Nos. 6+5+4+3..........	44.78	92.94
Nos. 1+2+3+4+5........	55 86	93.50	Nos. 6+5+4+3+2.......	57.46	93.17
Nos. 1+2+3+4+5+6.....	66.08	93.29	Nos. 6+5+4+3+2+1....	66.08	93.29

Original mixture (refractive index = 1.39651)............. 79.02% acetone
Corresponding vapor (by extrapolation)................... 94.10% acetone
Residue (refractive index = 1 41311).................... 67.87% acetone
Corresponding vapor (by extrapolation).................. 91.70% acetone

TABLE XXXIV.—RUN D.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % of acetone.
1........................	9.90	1.37534	91.23
2........................	10.22	1.37558	91.10
3........................	10.57	1.37651	90.61
4........................	11.84	1.37790	89.88
5........................	12.00	1.37950	89.01
6........................	12.12	1.38167	87.82

TABLE XXXV.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)
No. 1...	9.90	91.23	No. 6.....................	12.12	87.98
Nos. 1+2............ ..	20.12	91.17	Nos. 6+5...............	24.12	88.41
Nos. 1+2+3..............	30 69	90.98	Nos. 6+5+4...............	35.96	88.90
Nos. 1+2+3+4..........	42.53	90.68	Nos. 6+5+4+3.............	46.53	89.29
Nos. 1+2+3+4+5.......	54.53	90.31	Nos. 6+5+4+3+2.........	56.75	89.62
Nos. 1+2+3+4+5+6.....	66.65	89.86	Nos. 6+5+4+3+2+1......	66.65	89.86

Original mixture (refractive index = 1 41202)............. 68.64% acetone
Corresponding vapor (by extrapolation)................... 91.55% acetone
Residue (refractive index = 1.43452).................... 51.85% acetone
Corresponding vapor (by extrapolation).................. 87.00% acetone

TABLE XXXVI.—RUN E.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % acetone.
1........................	10.44	1.38191	87.68
2........................	12.12	1.38280	87.20
3........................	11.52	1.38470	86.10
4........................	11.56	1.38499	85.95
5........................	11.46	1.38965	83.22
6........................	11.80	1.39312	81.11

TABLE XXXVII.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)	Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)
No. 1.....................	10.44	87.68	No. 6.....................	11.80	81.11
Nos. 1+2..........	22.56	87.42	Nos. 6+5	23.26	82.10
Nos. 1+2+3.............	34.08	86.98	Nos. 6+5+4..............	34.82	83.43
Nos. 1+2+3+4..........	45.64	86.72	Nos. 6+5+4+3............	46.34	84.10
Nos. 1+2+3+4+5.......	57.10	86.03	Nos. 6+5+4+3+2.........	58.46	84.75
Nos. 1+2+3+4+5+6.....	68.90	85.20	Nos. 6+5+4+3+2+1..	68.90	85.20

Original mixture (refractive index = 1.42767)........ ....   57.15% acetone
Corresponding vapor (by extrapolation)................ ..   88.30% acetone
Residue (refractive index = 1.45463) ....   35.43% acetone
Corresponding vapor (by extrapolation)....... . ...   80.15% acetone

TABLE XXXVIII.—RUN F.

No. of distillate.	Weight of istillate ms.	Index of refraction.	Molar % of acetone.
1........................	4.58	1.39302	81.16
2........................	5.71	1.39574	79.49
3........................	3.85	1.39943	77.18
4........................	5.80	1.39943	77.18
5........................	3.44	1.40041	76.54
6........................	3.80	1.40247	75.19

TABLE XXXIX.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)
No. 1...	4.58	81.15
Nos. 1+2..........................	10.29	80.23
Nos. 1+2+3........................	14.14	79.41
Nos. 1+2+3+4......	19.94	78.77
Nos. 1+2+3+4+5.................. .	23.38	78.44
Nos. 1+2+3+4+5+6....	27.18	77.99

Original mixture (refractive index = 1.45143)..............   38.29% acetone
Corresponding vapor (by extrapolation)........ ....   81.1 % acetone

The residue in this case could not be analyzed.

TABLE XL.—RUN G.

No. of distillate.	Weight of distillate. Grams.	Index of refraction.	Molar % of acetone.
1........................	3.04	1.42067	62.40
2........'................	4.27	1.42267	60.92
3........................	5.53	1.42762	57.18
4........................	4.74	1.43197	53.83
5........................	4.33	1.43518	51.33
6........................	5.79	1.43994	47.55

TABLE XLI.

Distillates combined.	Combined weight. Grams.	Combined composition. (Molar % acetone.)
No. 1.............................	3.04	62.39
Nos. 1+2..........................	7.31	61.54
Nos. 1+2+3........................	12.84	59.68
Nos. 1+2+3+4.....................	17.58	58.14
Nos. 1+2+3+4+5...................	21.91	56.83
Nos. 1+2+3+4+5+6................	27.70	54.95

Original mixture (refractive index = 1.47359)..............   18.70% acetone
Corresponding vapor (by extrapolation)...................   63.60% acetone

The residue in this case could not be analyzed

TABLE XLII —RUN H

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of acetone
1	5 36	1 44386	44 38
2	3 86	1 44838	40 70
3	5 99	1 45233	37 37
4	5 90	1 45547	34 72
5	4 94	1 45898	31 70
6	6 64	1 46340	27 88
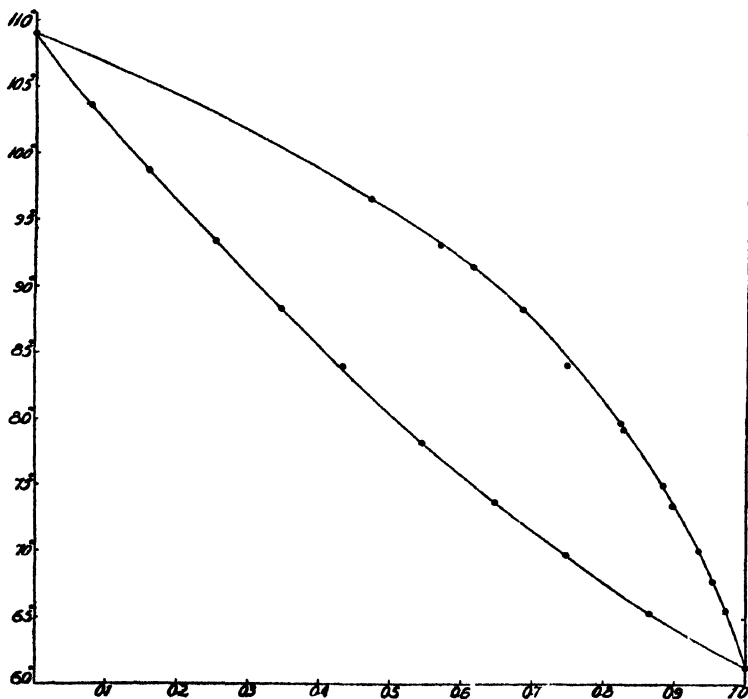
Fig 6 —Chloroform —toluene

TABLE XLIII

Distillates combined	Combined weight Grams	Combined composition (Molar % acetone)
No 1	5 36	44 38
Nos 1+2	9 22	42 85
Nos 1+2+3	15 21	40 73
Nos 1+2+3+4	21 11	39 08
Nos 1+2+3+4+5	26 05	37 71
Nos 1+2+3+4+5+6	32 69	35 78
Original mixture (refractive index = 1 48221)		10 77% acetone
Corresponding vapor (by extrapolation)		44 90% acetone

The residue in this case could not be analyzed

The results of all measurements in the case of acetone—toluene are exhibited by the curves of Fig 6

Section IX.—Results for Ethyl Iodide – Ethyl Acetate.

TABLE XLIV —RUN A

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of C_2H_5I
1	14 21	1 38261	12 78
2	11 90	1 38246	12 64
3	12 56	1 38210	12 28
4	12 50	1 38167	11 86
5	13 13	1 38133	11 55
6	11 66	1 38106	11 28
7	12 62	1 38053	10 76

TABLE XLV

Distillates combined	Combined weight Grams	Combined composition (Molar % C_2H_5I)	Distillates combined	Combined weight Grams	Combined composition (Molar % C_2H_5I)
No 1	14 21	12 78	No 7	12 62	10 76
Nos 1+2	26 11	12 72	Nos 7+6	24 28	11 01
Nos 1+2+3	38 67	12 57	Nos 7+6+5	37 41	11 20
Nos 1+2+3+4	51 17	12 40	Nos 7+6+5+4	49 91	11 36
Nos 1+2+3+4+5	64 30	12 3	Nos 7+6+5+4+3	62 47	11 55
Nos 1+2+3+4+5+6	75 96	12 08	Nos 7+6+5+4+3+2	74 37	11 72
Nos 1+2+3+4+5+6+7	88 58	11 89	Nos 7+6+5+4+3+2+1	88 58	11 89

Original mixture (refractive index 1 378 5)   9 01 C_2H_5I
Corresponding vapor (by extrapolation)   12 35° C_2H_5I
Residue (refractive index = 1 37678)   7 05° C_2H_5I
Corresponding vapor (by extrapolation)   10 43 % C_2H_5I

TABLE XLVI   RUN B

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of C_2H_5I
1	10 93	1 39167	21 26
2	16 39	1 39158	21 15
3	15 03	1 39080	20 47
4	14 64	1 39023	19 94
5	15 64	1 38956	19 35
6	19 62	1 38870	18 55

TABLE XLVII

Distillates combined	Combined weight Grams	Combined composition (Molar % C_2H_5I)	Distillates combined	Combined weight Grams	Combined composition (Molar % C_2H_5I)
No 1	10 93	21 26	No 6	19 62	18 55
Nos 1+2	27 32	21 19	Nos 6+5	35 26	18 91
Nos 1+2+3	42 95	20 93	Nos 6+5+4	49 90	19 21
Nos 1+2+3+4	57 59	20 68	Nos 6+5+4+3	65 53	19 51
Nos 1+2+3+4+5	73 23	20 39	Nos 6+5+4+3+2	81 92	19 83
Nos 1+2+3+4+5+6	92 85	20 00	Nos 6+5+4+3+2+1	92 85	20 00

Original mixture (refractive index = 1 38589)   15 90% C_2H_5I
Corresponding vapor (by extrapolation)   21 75% C_2H_5I
Residue (refractive index = 1 38242)   12 59% C_2H_5I
Corresponding vapor (by extrapolation)   18 00% C_2H_5I

TABLE XLVIII —RUN C

No of distillate	Weight of distillate Grams	Index of refraction	Molar % of C₂H₅I
1	16 59	1 40119	29 74
2	16 88	1 40070	29 31
3	14 76	1 39992	28 63
4	12 29	1 39943	28 21
5	16 91	1 39884	27 68
6	15 49	1 39802	26 96

TABLE XLIX

Distillates combined	Combined weight Grams	Combined compo sition (Molar % C₂H₅I)	Distillates combined	Combined weight Grams	Combined compo sition (Molar % C₂H₅I)
No 1	16 59	29 74	No 6	15 49	26 96
Nos 1+2	33 47	29 52	Nos 6+5	32 40	27 33
Nos 1+2+3	48 23	29 25	Nos 6+5+4	44 69	27 57
Nos 1+2+3+4	60 52	29 04	Nos 6+5+4+3	59 45	27 84
Nos 1+2+3+4+5	77 43	28 74	Nos 6+5+4+3+2	76 33	28 16
Nos 1+2+3+4+5+6	92 92	28 44	Nos 6+5+4+3+2+1	92 92	28 44

Original mixture (refractive index = 1 39390)   23 26% C₂H₅I
Corresponding vapor (by extrapolation)   30 10% C₂H₅I
Residue (refractive index = 1 39013)   19 87% C₂H₅I
Corresponding vapor (by extrapolation)   26 42% C₂H₅I
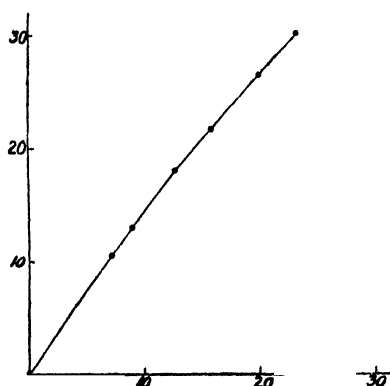
Fig 7.—Ethyl iodide—ethyl acetate
Abscissae = molar per cents ethyl iodide in liquid
Ordinates = molar per cents ethyl iodide in vapor

The results in the case of ethyl iodide —ethyl acetate are exhibited by the curve of Fig. 7, in which the abscissae show the composition of the liquid and the ordinates that of the corresponding vapor   Owing to lack of material, only three runs were made in this case, yielding six points, within a range of about 25% of iodide in the liquid phase.

Section X.—The Boiling Temperatures of the Mixtures.

The boiling point curve of mixtures of carbon disulfide and carbon tetrachloride, shown in Fig. 3, is based on measurements (under 760 mm.) reported in an older communication.[1]   The curves for chloroform—toluene (Fig. 5) and acetone—toluene (Fig. 6) reproduce observations tabulated below.   In the course of these observations, carried out with the aid of an Oddo ebullioscope and standardized thermometers, the barometric pressure varied irregularly within one or two millimeters   No measures were taken to avoid this, since such variations of pressure could have no appreciable influence on the composition of the vapors.

[1] Rosanoff and Easley, Loc. cit., p. 982.

TABLE L.—BOILING POINTS OF MIXTURES OF CHLOROFORM AND TOLUENE.   BAR PRESSURE, 743.7 ± 2 mm

Molar % CHCl₃	Boiling point
0	108 92°
7 86	103 58
15 96	98 72
25 46	93 38
34 64	88.30
43.33	83 94
54.44	78 17
64 66	73 65
74 70	69 67
86 54	65 35
100	61 33

TABLE LI.—BOILING POINTS OF MIXTURES OF ACETONE AND TOLUENE   BAR PRESSURE, 751 3 ± 0 2 mm

Molar % (CH₃)₂O	Boiling point
0	109 43°
14 99	88 28
34 63	74 93
51 42	68 77
65 98	64 37
78 71	61 22
89 99	58 71
100	56 50

Summary.

A method and apparatus are described for determining the composition of vapors in equilibrium with liquid mixtures; the method is rapid and requires no special experience on the part of the manipulator.   Also, results of measurements are given for the following four cases.   Carbon disulfide—carbon tetrachloride, chloroform—toluene, acetone—toluene, and ethyl iodide—ethyl acetate.   These data were needed here in connection with a study of fractional distillation, and the measurements were therefore carried out isopiestically, under ordinary atmospheric pressure.

WORCESTER, MASS

THE FREEZING POINT OF BENZENE AS A FIXED POINT IN THERMOMETRY.

By THEODORE W. RICHARDS AND JOHN W SHIPLEY
Received July 3, 1914

The transition temperatures of hydrated crystalline salts probably afford the most convenient and exact means of fixing points on the thermometric scale between 0° and 100° C.   A number of these have been determined in this laboratory, chief among which are the transition temperature for sodium sulfate,[1] the dekahydrate of sodium chromate into hexahydrate and into tetrahydrate,[2] the dihydrate of sodium bromide into the anhydrous salt,[3] the transition of manganese chloride from the tetra-

[1] Richards, Am. J. Sci. (1898); Richards and Wells, Proc Am Acad., 38, 431 (1902).
[2] Richards and Kelley, Ibid., 47, 171 (1911); THIS JOURNAL, 33, 847 (1911)
[3] Richards and Wells, Proc. Am. Acad., 41, 435 (1906).

hydrate into the dihydrate,[1] and the transition of dekahydrated sodium carbonate into the heptahydrate.[2] These points are perfectly definite, subject to no appreciable change by ordinary changes in atmospheric pressure, and usually involve considerable latent heat of transition. Most of them are easily reproducible. For these reasons they are very useful in calibrating thermometers.

The use of the freezing points of liquids for determining fixed points on the thermometric scale probably comes next to transition temperatures in regard to convenience. Freezing points, like transition temperatures, are more constant than boiling points, because the influence of change in atmospheric pressure is usually negligible On the other hand, however, the purity of the substance chosen becomes a very important issue.[3] Most liquids (except water and mercury) are very difficult to prepare in a pure state; and volatile impurities which scarcely affect the boiling point may very seriously change the freezing point. For this reason, the transition temperatures of pure salts are often preferable, such a substance as sodium sulfate is very easily purified by crystallization.

In other respects the errors to which the two types of equilibrium are subject are very similar. Both are liable to supercooling or superheating in the hands of the incautious experimenter, but in both, these sources of error are easily and completely eliminated by the use of plenty of each phase concerned, by proper protection of the system from gain or loss of heat with the help of an air-jacket and a like surrounding temperature, and by adequate but not too violent stirring. In both, the point is sharper and more accurate the greater the latent heat of melting. This is not only because outside heating or cooling is more quickly taken up, when this is large, but also because the influence of foreign substances on the freezing point is inversely proportional to the latent heat of fusion, provided that the crystals are uncontaminated by solute. This is expressed by a transposition of the well-known equation of van't Hoff, $\Delta T = RT^2/Mwl$, which gives the depression produced by 1 gram of dissolved substance of molecular weight M dissolved in w grams of solvent having a latent heat of fusion l per gram. The following table, therefore, shows that, whereas benzene is a good substance for this purpose, such substances as cyclohexane and cyclohexanol (especially the latter) are very unsuitable.

LATENT HEAT OF FUSION OF FOUR SUBSTANCES

Water	79 8 cal per gram
Benzene	30 1 cal per gram
Cyclohexane	8 8 cal per gram
Cyclohexanol	2 94 cal per gram

[1] Richards and Wrede, *Ibid*, **43**, 343 (1907) (Univ of Berlin)

[2] Richards and Fiske, THIS JOURNAL, **36**, 486 (1914)

[3] Landolt, "Über die genaue Bestimmung des Schmelzpunktes organischer Substanzen," *Z. physik. Chem*, **4**, 349 (1889).

The presence of 0.001% of water lowers the freezing point of cyclohexanol by 0.02°,[1] whereas the same amount of this impurity affects the freezing point of benzene by less than 0.002°.[2]

Another property adds to the satisfactory nature of benzene for this purpose, namely, the possibility of freeing it from most of its impurities by fractional crystallization or freezing. Thiophene, it is true, cannot be separated in this way, but this impurity may easily be removed chemically. On the other hand, paraffin hydrocarbons, olefines, acetone, and most other impurities are quickly eliminated from the successive crops of crystals.

The fact that the melting point of these crystals is 5.5° above that of water—just the length of the usual Beckmann scale - makes it an especially useful fixed point, for, with the help of these two melting points, any such thermometer may be easily standardized, and then, with the help of the well-known correction factor, used with confidence at any other temperature—provided that due precautions be taken for correcting the result for the temperature of the exposed thread.

For these reasons it seemed to us worth while to make a careful study of this point, especially because the published work of others is conflicting with regard to it. Paterno[3] gives three values, 5.53°, 5.55°, and 5.48°, while Lachowicz[4] gives 5.42°, and Young,[5] 5.58°. The discord among these and other values is probably due to inaccurate thermometry.

As many of the observers were principally concerned with the purity of their benzene rather than with its absolute freezing point, the constancy of the melting temperature and not its exact value was all that was needed, but of course for other purposes the exact point must be known.

. Dr. F. Barry, in 1910, and Dr. H. S. Davis, in 1913, under the direction of one of us, prepared benzene in a very pure state in order to determine its heat of combustion as a standard of comparison for other organic substances. Their final values, as determined by our best thermometers, were 5.484° and 5.486°, respectively. These results were entirely independent, as the necessary corrections had not been applied to the earlier thermometric readings when the later ones were made. Both experimenters determined the ice point on standard thermometers immediately after taking the melting point of the benzene. Neither of these investigations have as yet been published, but they will soon appear in print.

From this earlier work it was apparent that the true freezing point of

[1] Richards and Shipley, in a research as yet unpublished.

[2] Hertz, *Ber.*, **31**, 2669 (1898).

[3] Paterno, *Gazz. chim. ital.*, **27**, I, 481–536 (1897).

[4] Lachowicz, *Ber.*, **21**, 2206 (1888).

[5] Young, *Proc. Roy. Soc. Dublin*, **12**, 31, 385 (1910); *Trans. Chem. Soc.*, **40**, 486 (1899). Professor Young, in private correspondence, has stated that not much pains had been spent upon thermometric precautions in his work. We are much obliged to him for the trouble he has taken in consulting his original records.

benzene probably lies between 5.48° and 5.50° with indication of the value 5.485°; yet more exhaustive work was needful in order to permit its use as a fixed point in thermometry.   For this purpose we deemed it advisable to obtain benzene from two entirely different sources.   Commercial "c. p." benzene procured from the distillation of a Pennsylvania coal-tar was the starting point for one preparation, and another specimen consisted of benzene prepared synthetically from benzoic acid by a well-known German firm.   The two samples were carried through the same process of purification as follows:

(*a*) About 600 cc. of the benzene were shaken with clean mercury.   No darkening of the surface of the mercury was observed.

(*b*) The benzene was next shaken on a shaking machine (about 2.5 hours each time) with six successive quantities of concentrated sulfuric acid.   The acid was deeply blackened by the first four treatments, indicating the presence of substances charred by the action of strong acid, but the last two showed only a slight yellow coloration.

(*c*) The benzene was next washed with two quantities of water and then shaken out with a concentrated solution of sodium hydroxide, followed by two more washings with water.

(*d*) Following this came another shaking out with mercury for about four hours.   A considerable blackening of the surface of the metal was observed.

(*e*) After washing several times with water, the benzene was dried over calcium chloride and sodium and distilled.   Almost all of the product came over within 0.05°; that fraction distilling between 80.15° and 80.18° (uncorrected) was preserved for further purification.

(*f*) The benzene was next recrystallized in porcelain, the coal-tar product six times, the synthetic five, and the fractions were preserved over sodium in glass bottles kept in the dark.   The sodium was freshly cut and allowed to stand for some time in the mother liquor of the second crystallization before being put through the sodium press.

Before determining the freezing point of the purified samples of benzene, the excellent Beckmann thermometer to be used was carefully compared with a standard instrument, Baudin No. 15200, which had been standardized by the Bureau International des Poids et Mesures in Paris, and frequently used for the most accurate thermometric work in this laboratory.[1] The Beckmann' thermometer (P. T. R. 31827) was graduated in hundredths and covered a scale of six degrees, the length of a degree being 3.8 cm. It had been calibrated by the Physikalisch-Technische Reichsanstalt, Berlin, in 1907. . The comparison of the instruments was carried out in collaboration with Dr. T. Thorvaldson, to whom we wish to express our gratitude for his kind assistance.   The thermometers were compared at

[1] See *Proc. Am. Acad.*, **38**, 434 (1902); *Z. physik. Chem.*, **44**, 467 (1903).

two points: the ice point of benzene and the ice point of water. The benzene used was commercial c. p. benzene distilled and dried over sodium. Since the determinations were for comparative purposes only, the purity of the benzene was not yet in question, but the ice point of water was, of course, carefully determined immediately afterwards under precisely parallel conditions.

The readings were taken immediately after vigorous stirring of the mixture and the two thermometers were read practically simultaneously. The measurement of the temperatures was carried out in accordance with the precautions pointed out by one of us in a recent publication.[1]

In this way it was found that a range of $5.125°$ on the Beckmann corresponds to $5.104°$ as read on the corrected standard Baudin; or $1.000°$ as read on the former over this range of temperature corresponds to $0.9958°$ on the hydrogen scale. This was essentially the value given by the Reichsanstalt for this thermometer under these conditions.

The Beckmann apparatus was used in the freezing point determinations, about 30 g. of substance being employed. The apparatus was swept with a current of air dried with sulfuric acid and the benzene was distilled directly into the apparatus through the side tube, the thermometer and stirrer being already in place. The first third of the distillate was rejected. During the distillation, as well as during the determination, a slow current of dry air was allowed to pass in through the side tube, thus preventing the access of moisture from the atmosphere. Such contamination was especially liable to happen during the operation of stirring. The benzene-ice was present in varying quantities and conditions. The most satisfactory mixture was obtained by subcooling the liquid several degrees, and then, by vigorous agitation, producing a large crop of finely divided crystals. It was found, however, that so long as plenty of crystals were present, the outside bath was not too cold, and adequate stirring was employed, the same constant freezing point was obtained with both finely divided and large crystals. The purity of the benzene was indicated by the constancy of the freezing point with diminishing proportion of mother-liquor, as the freezing progressed. Great constancy was observed in the fifth and sixth crystallizations of the coal-tar product, and in the fourth and fifth of the synthetic benzene.

Immediately after determining the freezing point of benzene, the ice point of water was taken in the same apparatus. Freshly distilled water was boiled and frozen under a variety of conditions; constant results were obtained with the same precautions as in the case of benzene; and this outcome was confirmed by the immersion of the instrument in a large bath of pure ice and water.

[1] Richards, "The Measurement of Temperature in the Operations of Analytical Chemistry," *Orig. Comm. 8th Congress of Applied Chem.*, 1912.

The ice points of water and benzene were thus observed in the same apparatus in the same way and with the same depth of immersion of the bulb and the same length of mercury column exposed to room temperature. The only stem correction necessary was that for the difference between the room temperature and the temperature of the freezing point of benzene, applied to the number of degrees between the ice point of water and of benzene.

The samples used in each trial were as follows.

A Coal-tar benzene, 5th recrystallization
B Coal-tar benzene, 6th recrystallization
C Synthetic benzene, 4th recrystallization
D Synthetic benzene, 5th recrystallization
E Coal-tar benzene, 5th recrystallization

Table I summarizes the results with the Beckmann thermometer P. T. R. No 31827.

TABLE I

Sample	Constant Beckmann reading	Ice point	Difference	Total correction [1]	True temp
A	5 822	0 300°	5 522	—0 038	5 484°
B	5 821	0 300°	5 521	—0 038	5 483°
C	5 772	0 249°	5 523	—0 038	5 485°
D	5 772	0 249°	5 523	—0 038	5 485°
E	5 760	0 237°	5 523	—0 038	5 485°

Average = 5 484°

Trials A and B were made on the same day, C and D were made about four weeks afterward, and E was made yet three weeks later. These tests show: first, that the coal-tar material (A, B and E) was essentially identical (at least as regards melting point) with the synthetic material, and secondly, that further recrystallization caused no change in the value Hence, the presumption is that these results give the true value corresponding to the pure substance.

Although these results are very concordant and indicate that the freezing temperature of benzene affords an accurate point for thermometric work, it was deemed advisable to take a series of observations directly on a Baudin standard instrument, in order to verify the absolute value of the above series of results. A shorter wide test tube was substituted for the inside tube of the Beckmann apparatus, and through the cork of this test tube passed the Baudin thermometer, No. 15200, and a narrower tube for the stirrer. This latter had a side arm, through which a current of dry air passed during the determination. The tube was submerged in the cool outside bath to within 0.5 cm. of the bottom of the cork, and the

[1] This correction was in each case —0 023 for the fundamental interval (1 000° on the thermometer = 0 9958 true degrees) and —0 015 for the 5 50 stem exposed to the constant room temperature 23° or —0 038 in all

reading of the Baudin was made through the glass almost at the surface of this bath By this means the necessity for any stem correction was obviated The ice point of water was taken immediately afterwards in the same apparatus with the same precautions Four determinations were made on three successive days, the last two being made on the same day The readings were verified in each case by Dr Thorvaldson In Table II, each observed reading listed is the average of a number of independent observations not varying between the extremes by more than 0 003° The barometer readings for three days varied by only 3 mm , the readings being 763 mm , 762 mm , and 765 mm , respectively Since the bulb of the thermometer was immersed to the same depth in each determination, the effect of the exterior pressure was identical in all four cases The conditions of the experiments were so chosen that all other corrections were necessarily invariable

TABLE II
Corrections to be Applied

	At ice point benzene	At ice point water
Calibration	$+0 003$	$+0 002$
Interior pressure	$+0 015$	$+0 009$
Exterior pressure	$-0 001$	$-0 00$
Fundamental interval	$+0 004$	$\pm 0 000$
Stem	$\pm 0 000$	$+0 000$
Total correction	$+0 041°$	$+0 010$

Final Readings Observed and Corrected

Determination	Benzene			Water		
	Observed melting point	Corr	Corr reading	Observed ice point	Corr	Corr reading
F	$+5 688°$	$+0 041°$	$5 729°$	$0 208°$	$0 010$	$0 218°$
G	$5 686$	$+0 041°$	$5 727°$	$0 207°$	$0 010$	$0 217°$
H	$5 688°$	$+0 041°$	$5 729°$	$0 207°$	$0 010$	$0 217°$
I	$5 689°$	$+0 041°$	$5 730°$	$0 207°$	$0 010$	$0 217°$

Determination	Benzene melting point corr reading	Water ice point corr reading	F pt benzene	Hyd scale corr	F pt benzene hyd scale
F	$5 729°$	$0 218°$	$5 511°$	$-0 030$	$5 481°$
G	$5 727°$	$0 217°$	$5 510°$	$-0 030$	$5 480°$
H	$5 729°$	$0 217°$	$5 513°$	$-0 030$	$5 482°$
I	$5 730°$	$0 217°$	$5 513°$	$-0 030$	$5 483°$

Averages 5 482°

This compares very satisfactorily with the values previously found, as follows

	Average values	Variation from mean	Maximum variation between extremes
Beckmann	$5 484°$	$0 001$	$0 002$
Baudin	$5 482°$	$0 002$	$0 003$

The true freezing point of benzene may then be safely taken as 5.483°.
This is only 0.001° different from the result of Barry, and 0.003° different
from the latest and best trials of Davis.

The wide deviations of others are probably to be referred chiefly to
doubtful thermometry, for benzene is evidently not very difficult to obtain
in a pure state.

These experiments show that the freezing point of pure benzene, 5.483°,
is attained so easily that it may be used as a very satisfactory fixed point
in thermometry; and taken in connection with the freezing point of water,
about 5.5° below, may afford an excellent means of fixing two points on a
Beckmann thermometer.

The authors are glad to express indebtedness to the Carnegie Institution
of Washington for generous support in this investigation.

Summary.

The results of this research may be summed up as follows:

(1) Benzene pure enough for the purpose in hand is not difficult to
prepare.

(2) With due precautions in the thermometric measurements a very
definite freezing point is given by benzene. The true value is determined
by constancy after repeated fractional crystallization.

(3) The freezing point of benzene is 5.483° ± 0.002° on the international
hydrogen scale.

(4) This fixed temperature may be advantageously used, in connection
with the ice point of water, for calibrating Beckmann thermometers.
Especial attention must be paid to the temperature of the exposed column
in correcting this interval for use at other temperatures.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY]

ON THE ABSORPTION OF GLUCOSE BY BONE-BLACK.

[PRELIMINARY COMMUNICATION.]

BY HAROLD A. MORTON.

In connection with a study of the mutarotation and specific rotatory
power of the sugars, I have been obliged to purify a considerable quantity
of glucose. Using bone-black as a decolorizer, I observed that a surpris-
ingly large quantity of the sugar was extracted by the bone-black from
the aqueous solution. It appeared interesting to investigate the phe-
nomenon systematically, the question being whether the partition of
the sugar does not follow some simple principle, like the distribution law.

Preliminary experiments soon indicated that at ordinary temperatures
the process of absorption is exceedingly slow, and that, to obtain results
within a reasonable time, it would be best to employ a temperature of
about 80°. In the experiments described below, a Freas constant tem-

perature oven was employed. The tubes containing the mixtures were kept within the oven in a large bath of water covered with a layer of oil.   In this manner it was possible, throughout the experiments, to maintain a temperature of 80 6°, the variations from which at no time exceeded 0.2°. The glass tubes in which the experiments were carried out had a capacity of about 35 cc. Into each tube was introduced a carefully weighed amount (about 3 5 g.) of bone-black and a measured volume (in most cases 23 cc.) of sugar solution. The tube was then sealed off, the bone-black more or less evenly distributed throughout the solution by gentle tapping, and the tube placed horizontally in the bath.   In some cases two, in others three, tubes of the identical make-up were used, to permit of testing the attainment of equilibrium by abandoning the tubes for different lengths of time.   Preliminary experiments had indicated that as 80° equilibrium is not attained in less than six days, and consequently, as the tables show, none of the tubes were removed for examination in less than this time. In most cases equilibrium was attained after about ten days of heating.

Ordinary distilled water was employed without further purification. The sugar was purified by recrystallization of pure anhydrous glucose from water at ordinary temperatures; the resulting monohydrate, after being air-dried, was used as such for making up solutions of approximately the desired strength.   The exact strength of the solutions was then determined polarimetrically on the basis of Tollens's measurements.[1]

Preliminary experiments having indicated that no commercial bone-black could be relied on to be sufficiently pure, Kahlbaum's best bone-black was subjected to a somewhat laborious process of purification. It was first stirred for several hours in a large volume of nearly boiling 2% nitric acid, then the process was repeated with a fresh lot of nitric acid, next the bone-black was similarly treated with 2% solutions of sodium carbonate, and finally all soluble salts were thoroughly washed out by stirring with large amounts of distilled water. On filtering off the last wash-water, the mass was carefully dried.

After the requisite time of heating in the thermostat, each tube was opened and its contents filtered through a layer of asbestos in a Gooch crucible, care being taken not to lose any of the filtrate, which was weighed. In this manner it was learned what weight had been lost by absorption in the bone-black. The filtrate being thereupon analyzed polarimetrically, it further became clear how much sugar and also how much water had been taken up by the bone-black. The method is obviously not very precise, for in spite of all effort a certain amount of the solution was partly lost, partly retained mechanically by the bone-black, but fortunately the inaccuracy has not been such as to obscure the law which apparently

[1] Tollens. *Ber.*, 9. 1535 (1876).

TABLE I

	Series I Tube No			Series II Tube No		Series III Tube No.		Series IV Tube No		
	I	II	III	I	II	I	II	I	II	III
Weight of bone black	3·51 —	3·51	3·40	3·50	3·50	3·52	3·51	3·52	3·51	3·49
Original weight of solution	28·14	27·75	23·32	24·30	24·26	24·66	24·73	25·15	25·24	25·03
Original angle a (circular degrees)	4·976	4·976	4·976	14·898	14·898	20·232	20·232	26·258	26·258	26·258
Original percentage glucose in solution	4·630	4·630	4·630	13·338	13·338	17·748	17·748	22·507	22·507	22·507
Original weight of glucose in solution	1·303	1·285	1·080	3·242	3·236	4·377	4·389	5·661	5·681	5·634
Time of heating (hours)	144	174	262	171	265	172	266	148	196	269
Final weight of solution	24·8	23·6	19·2	20·3	20·5	20·6	20·3	21·2	20·8	20·4
Final angle a (circular degrees)	4·039	4·022	3·856	13·108	12·673	18·477	17·745	24·537	24·157	23·356
Final percentage of glucose in solution	3·771	3·756	3·603	11·818	11·444	16·320	15·716	21·171	20·876	20·243
Final weight of glucose in solution	0·935	0·886	0·692	2·399	2·346	3·362	3·190	4·488	4·342	4·130
Final weight of glucose per 1 g solution (c_1)	0·0377	0·0375	0·0360	0·1182	0·1144	0·1632	0·1572	0·2117	0·2088	0·2024
Total weight of glucose in bone black	0·368	0·399	0·388	0·843	0·890	1·015	1·199	1·173	1·339	1·504
Weight of glucose per 1 g bone-black (c_2)	0·105	0·113	0·112	0·241	0·254	0·288	0·341	0·333	0·381	0·431
Weight of glucose per 1 g solution / Weight of glucose per 1 g bone black $= \dfrac{c_1}{c_2}$		0·33	0·32		0·45		0·46		0·47	

	Series V Tube No			Series VI Tube No		Series VII Tube No		
	I	II	III	I	II	I	II	III
Weight of bone-black	3 51	3 53	3 52	3 51	3 51	3 52	3 52	3 52
Original weight of solution	26 49	26 42	26 58	27 43	27 62	28 21	28 49	28 37
Original angle a (circular degrees)	42 635	42 635	42 635	57 837	57 837	68 312	68 312	68 312
Original percentage of glucose in solution	34 417	34 417	34 417	44 327	44 327	50 578	50 578	50 578
Original weight of glucose in solution	9 117	9 093	9 148	12 159	12 243	14 268	14 410	14 349
Time of heating (hours)	149	237	262	150	245	151	243	285
Final weight of solution	22 2	21 5	21 6	21 7	22 0	22 4	22 1	22 3
Final angle a (circular degrees)	39 242	39 145	38 661	54 409	52 772	64 505	62 916	62 860
Final percentage of glucose in solution	32 062	31 994	31 653	42 183	41 145	48 361	47 410	47 376
Final weight of glucose in solution	7 118	6 879	6 837	9 154	9 052	10 833	10 478	10 565
Final weight of glucose per 1 g solution (c_1)	0 3206	0 3199	0 3165	0 4218	0 4115	0 4836	0 4741	0 4738
Total weight of glucose in bone-black	1 999	2 214	2 311	3 005	3 191	3 435	3 932	3 784
Weight of glucose per 1 g bone-black (c_2)	0 570	0 627	0 656	0 856	0 909	0 976	1 117	1 075
$\dfrac{\text{Weight of glucose per 1 g solution}}{\text{Weight of glucose per 1 g bone-black}} = \dfrac{c_1}{c_2}$			0 48		0 45		0 42	0 44

governs the results. The analyses were carried out with the aid of an excellent Lippich saccharimeter made by Schmidt and Haensch. The Ventzke degrees originally read off were changed into circular degrees, and, further, all angles given in the tables are based on readings obtained with a 2 decimeter tube.

The concentrations of the seven series of glucose solutions studied ranged from 4.63% to 50.58%, so that the regularity exhibited by the results can hardly be accidental. The results are fully reproduced in the tables, which will explain themselves.

The results of Series I to VII in Table I would seem to indicate that the absorption of glucose from aqueous solution follows a principle very like the distribution law. In these preliminary experiments, it was not possible to undertake a determination of the specific volume of the bone-black after it had taken up sugar, in order to ascertain the volume-concentration of sugar in the bone-black. The distribution law in its ordinary form could, therefore, not be tested. On the other hand, it was possible to compare the ratios of the weight of sugar per gram of solution to that per gram of bone-black in the several experiments. The results are summarized in Table II, which shows that *those ratios are practically equal for the entire range of concentrations studied.* Thus the distribution law seems to hold true here in some approximate form.

TABLE II.

Original concentration of aqueous solution. Per cent.	c_1 (in liquid).	c_2 (in solid).	c_1/c_2.
4.63	0.0360	0.112	(0.32)
13.34	0.1144	0.254	0.45
17.75	0.1572	0.341	0.46
22.51	0.2024	0.431	0.47
34.42	0.3165	0.656	0.48
44.33	0.4115	0.909	0.45
50 58	0.4738	1.075	0.44

Mean, 0.46

The distribution constant 0.46 expresses the curious fact that when equilibrium has been attained the amount of sugar contained in a gram of bone-black is more than twice as great as that contained in a gram of solution, which would scarcely be expected.

But the data contained in the above tables indicate further that the bone-black had taken from the solutions, not only part of their glucose, but also part of the water. That the solution is not taken up by the bone-black without change, is shown by the observed change in rotation of the solutions. Table III shows the relative amounts of glucose and water in the bone-black and in the aqueous solution. The weight of glucose per 1 g. water in the bone-black is denoted by the symbol c'_1; the weight

of glucose per 1 g of water in the solution is denoted by c'_2 Leaving out of account the most dilute solution (Series I), the ratios c'_2/c'_1, shown by the last horizontal line in the table, may probably be considered as constant within the errors of experiment   However this be, the value of the ratio indicates that the solution within the bone black is at least twice as concentrated as the outside solution

TABLE III

	I	II	III	IV	V	VI	VII
				Series No			
Grams glucose in final solution	0 691	2 334	3 191	4 129	6 836	9 053	10 566
Grams water in final solution	18 5	18 1	17 1	16 3	14 8	12 95	11 73
Glucose per gram of water in the solution (c'_1)	0 037	0 129	0 186	0 254	0 463	0 699	0 900
Grams glucose in bone black	0 389	0 902	1 193	1 499	2 320	3 182	3 799
Grams water in bone black	3 71	3 00	3 21	3 10	2 68	2 42	2 30
Glucose per gram of water in the bone-black (c'_2)	0 105	0 301	0 372	0 484	0 865	1 316	1 65
Glucose per gram of water in bone-black / Glucose per gram of water in solution $= \dfrac{(c'_2)}{(c'_1)}$	(2.8)	2.3	2.0	1 9	1 9	1.9	1.8

It finally seemed interesting to inquire whether bone-black does not take up water according to some principle similar to that followed by its absorption of glucose   Table IV shows this to be the case.

TABLE IV

W_c Grams water per 1 g of bone black	W_s Grams water per 1 g of solution	W_c/W_s
1 07	0 96	1 1
0 86	0 89	1 0
0 91	0 84	1 1
0 89	0 80	1 1
0 76	0 68	1 1
0 69	0 59	1 2
0 65	0 52	1 2
		Mean, 1 1

It is my hope to continue these experiments under conditions permitting of greater precision of measurement, and to extend them to a number of other substances

It is a pleasure to express my gratitude to Professor M. A. Rosanoff for a number of helpful suggestions in connection with this work. Indirectly my thanks are also due to the National Academy of Sciences, for the use of instruments placed at the disposal of Professor Rosanoff and his students by the Committee of the Bache Fund.

WORCESTER, MASS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VOLUMETRIC ESTIMATION OF TITANIUM BY MEANS OF FERRIC CHLORIDE.

BY T R. BALL AND G. McP SMITH
Received June 30, 1914

The tedious operations involved in the quantitative separation of titanium from iron, aluminium, etc., render it desirable to find a convenient and reliable volumetric process for the direct determination of this element in the presence of the above mentioned substances.

With this end in view, various processes have been proposed for the volumetric estimation of titanium. All of these are based upon the fact that titanic salts are under certain conditions capable of being reduced quantitatively to salts of trivalent titanium, which, in turn, may readily be oxidized back to the tetravalent condition; as oxidizing agents for this purpose have been proposed, potassium permanganate, methylene blue, and ferric salts.

Owing to the difficulty experienced in titrating with permanganate in the presence of ferrous iron and hydrochloric acid, Wells and Mitchell[1] reduce the iron in sulfuric acid solution with hydrogen sulfide, and then titrate the iron alone with potassium permanganate. In the resulting solution they reduce the iron and the titanium with zinc, after which both metals are titrated with potassium permanganate. The titanium is, of course, gotten by difference. According to the authors, the results are always somewhat low.

In accordance with Wells and Mitchell, Newton[2] reduces the two metals in sulfuric acid solution with zinc, in an atmosphere of hydrogen. Then, however, in order to lessen as much as possible the oxidizing action of air on the solution during the subsequent operations, he adds an excess of ferric sulfate solution. In this way, the titanous sulfate present is at once oxidized at the expense of an equivalent quantity of the ferric iron, and the total ferrous iron in the resulting solution is titrated with potassium permanganate.[3]

[1] THIS JOURNAL, 17, 878 (1895).
[2] Am. J. Sci., 25, 130 (1908).
[3] According to either of these methods, it is necessary to correct for any iron which may be contained in the zinc. No such correction has to be made in the case of the methylene blue and ferric salt titration methods.

Neumann and Murphy[1] have recently investigated the use of methylene blue as an oxidizing agent for the direct titration of trivalent titanium in the presence of ferrous salts. In this case the methylene blue is decolorized and is therefore its own indicator. While the results obtained are very exact, the end point of the titration is rather slowly attained and is recognized best in a solution heated nearly to boiling, whose volume is about 150 cc., and to which a very considerable proportion of concentrated hydrochloric acid has been added. Furthermore, the standard solution of methylene blue does not retain its strength; it must occasionally be standardized against known quantities of freshly reduced titanium, and this also detracts somewhat from the convenience of the method.

E. Knecht, who first made use of titanous salts as reducing agents in organic chemistry,[2] has studied their action also upon certain inorganic salts. Knecht and Hibbert[3] have recommended the use of titanous chloride solutions for the volumetric estimation of ferric iron. The reaction is indicated by the equation:

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$
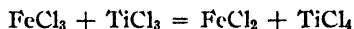
With potassium thiocyanate as an indicator, they were able to obtain very satisfactory results for iron, and their method has been found by others to give very exact results. In his original publication Knecht gives a single, somewhat low, result obtained by employing the reaction for the estimation of titanium.[4]

F. W. Hinrichsen[5] later determined titanium by means of ferric iron with results which he does not give, but which he says are satisfactory. As the reducing agent he recommends a 50% zinc-magnesium alloy in hydrochloric acid.

[1] Z. angew. Chem., 26, 613 (1913). Neumann and Murphy in their paper state the reaction to be that expressed by the "equation:"
$$C_{16}H_{18}N_3SCl + 2TiCl_3 + HCl = C_{16}H_{18}N_3S + 2TiCl_4.$$
The following equation is probably correct:
$$C_{16}H_{18}N_3SCl + 2TiCl_3 + 2HCl = C_{16}H_{20}N_3SCl + 2TiCl_4.$$
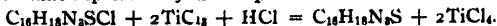
[2] Ber., 36, 166 (1903). The methylene blue reaction given above was discovered by Knecht.

[3] Ber., 36, 1549 (1903).

[4] Neumann and Murphy, loc. cit., claim that the degree of accuracy attainable by the methylene blue method is greater than that to be had by any other method for the determination of titanium, and that it is the only method which permits of the direct estimation of titanium in the presence of iron, silica, alumina, etc. While they mention the ferric salt method, they erroneously state that it can be used only in connection with "Rothe's ether method." These statements are justly criticized by Knecht (Z. angew. Chem., 26, 734 (1913)), but Knecht refers only to the work of Hinrichsen, without giving any additional data. In the determination of titanium by any of these volumetric methods, substances such as tin, chromium, vanadium, tungsten and molybdenum must of course be absent.

[5] Chem. Ztg., 31, 738 (1907).

G. Gallo[1] has also investigated the same method. He recommends that the reduction be carried out with zinc at $10°$ in rather strong sulfuric acid. His results are very good, but he allows 12 hours for the complete reduction of the titanium.

In view of the ease with which standard ferric salt solutions may be prepared and kept, as compared with those of titanous salts (which have to be preserved under carbon dioxide or some other inert gas, and which even then require frequent standardization), it seems strange that Knecht and Hibbert did not place especial emphasis upon the use of the above reaction for the determination of titanium, rather than for that of ferric iron.

Experimental.

Standard Titanium Sulfate Solution.—Exactly 6 g. of pure K_2TiF_6[2] were twice evaporated with sulfuric acid. The residue from the second evaporation was treated with a few cc. of sulfuric acid, and the mixture was then taken up with 5% sulfuric acid, of which a sufficient quantity was finally added to make the volume up to 1 liter.

The ignited precipitate obtained upon neutralizing 50 cc. of this solution with ammonia, adding acetic acid and sodium acetate, and boiling for several minutes, weighed 0.1002 g. (calculated weight = 0.1000 g. TiO_2).

A second, less concentrated, solution was prepared by making 100 cc. of the standard solution up to 1 liter with 5% sulfuric acid.

Standard Ferric Chloride Solution.—Pure ferric chloride was dissolved in water with the addition of enough hydrochloric acid to give a perfectly clear solution. The resulting solution was standardized by running 30 cc. portions of it from a buret, with stirring, into an excess of aqueous ammonia; in each case the precipitate was filtered off and ignited to constant weight. Two such determinations gave as normality factors 0.05043 and 0.05041; the mean of these was taken as correct.

A less concentrated solution was prepared by diluting 100 cc. of the standard solution to a volume of 500 cc. The normality of this solution was taken to be $0.05042 \div 5 = 0.010084$.

The indicator was a saturated solution of potassium thiocyanate, of which 1 cc. was used in each titration.

Zinc was found to be a satisfactory reducing agent. Several other metals were tried.

In all cases the titanous solution should be carefully guarded from oxidation by air after the reduction and during titration. In the determinations to be given below the solution was in most cases protected by an

[1] *Atti Roy. Acad. d Lincei*, [5] 16, I, 325–30; *Chem. Zentrlb.*, 1907, p. 1600.
[2] This salt was prepared by crystallizing three times in platinum pure $K_2TiF_6.H_2O$ from dilute hydrofluoric acid; the dried product was finally ignited in platinum.

ordinary Contat-Gockel valve.   This does very well if the solution is re-
duced in the cold, but with hot solutions the slightest cooling causes sodium
bicarbonate solution from the valve to enter the reduction flask.   While
small quantities of sodium bicarbonate do no harm, larger quantities
use up much of the acid and it might therefore be desirable to prevent
this feature altogether.   This may be accomplished by means of the modi-
fied valve shown in Fig. 1.

A   Glass Wool
B   Asbestos Filter
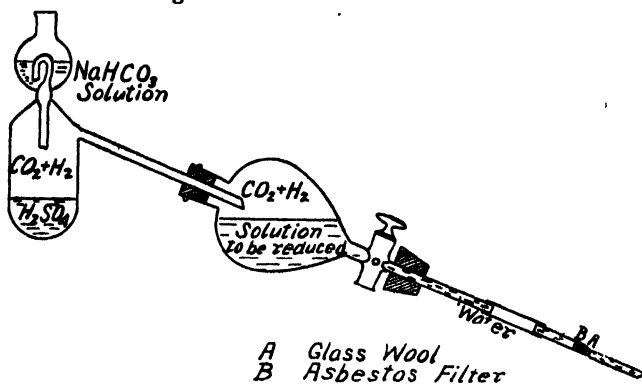
Fig. 1.

In carrying out the reduction with zinc, it is not always practicable
to completely dissolve the metal, and sometimes it is almost impossible
to do so.   The solution must be filtered therefore before titration from
the unused zinc, even when sheet or bar zinc is used.   Since the reduc-
tion can be carried out at room temperature, separatory funnels of 250
cc. capacity are recommended as containing vessels.   A glass tube of the
same diameter as the funnel stem and about 4 inches in length is drawn
out from its middle point, and upon the resulting constriction a small
mat of glass-wool and asbestos is placed, to serve as a filter.   A rubber
(suction-flask) stopper is fitted upon the stem of the funnel, and the filter
tube is then attached to the stem by means of rubber tubing.   Before be-
ginning a reduction, the funnel stem and filter tube are filled with freshly
boiled water, after which the strongly acid solution and a large excess of
zinc are introduced into the funnel; the air is displaced from the latter
by carbon dioxide from a generator, and the mouth of the funnel is then
fitted with a Contat-Gockel valve.[1]   The reduction is allowed to proceed
for about 2 hrs., after which the valve is removed and the solution is drawn
through the filter into a suction flask previously filled with carbon dioxide,
the funnel being washed out with freshly boiled water in such manner

[1] If the modified valve shown in the figure is used, it should be filled with carbon
dioxide just before being connected with the funnel.

as not to permit the entrance of any air into the funnel tube, the end of
the filter tube should reach to the bottom of the suction flask   After
the addition of the indicator, the reduced solution is rapidly titrated with
standard ferric chloride solution [1]

The apparatus used for carrying out the reduction is illustrated in Fig
1, in which the modified valve referred to above is shown, instead of the
ordinary Contat Gockel valve

The results obtained with the above solutions are given in Table I

<center>TABLE I [2]</center>

No	TiO₂ taken g	TiO₂ found g	Fe₂O₃ present before reduction g	Acid used		Temperature of reduction	Form of zinc
1	0 0600	0 0601	None	10 cc HCl (sp gr 1 19)		Boiling	Bar
2	0 0390	0 0389	None	10 cc HCl (sp gr 1 19)		Room	Granulated[3]
3	0 0500	0 0503	None	10 cc H₂SO₄ (1	1)	Boiling	Granulated
4	0 0500	(0 0486)	None	10 cc H₂SO₄ (1	1)	Boiling	Granulated
5	0 0500	0 0503	None	10 cc H₂SO₄ (1	1)	Room	Granulated
6	0 0500	0 0504	None	10 cc H₂SO₄ (1	1)	Room	Granulated
7	0 0200	0 0202	None	10 cc H₂SO₄ (1	1)	Room	Bar
8	0 0020	0 0020	0 1000	10 cc H₂SO₄ (1	1)	Room	Granulated
9	0 0100	0 0097	0 1328	10 cc H₂SO₄ (1	1)	Room	Granulated
10	0 0100	0 0097	0 1328	10 cc H₂SO₄ (1	1)	Room	Granulated
11	0 0200	0 0200	0 1328	10 cc H₂SO₄ (1	1)	Room	Granulated
12	0 0200	0 0199	0 1328	10 cc H₂SO₄ (1	1)	Room	Granulated

A sample of ilmenite, in which, by means of duplicate analyses accord
ing to the Gooch gravimetric method, 34 60% and 34 65% of TiO₂
were found, was also analyzed by the ferric chloride method

It is very difficult by means of the usual pyrosulfate fusion method to
get into solution substances such as ilmenite and other titaniferous iron

[1] It might be well, before beginning a reduction to place upon the asbestos filter
a little granulated zinc, and upon removing the valve at the end of the reduction to
introduce into the mouth of the funnel the open outlet tube of a carbon dioxide generator
furthermore, it would do no harm to pass carbon dioxide through the suction flask
during the titration   These precautions were however, omitted in the above work
and the results are nevertheless good

[2] All of the above titrations were made in the cold after having filtered the solution
from undissolved zinc into an atmosphere of carbon dioxide   In the determinations
in which the reduction was carried out at the boiling temperature, the solutions were
allowed to cool to room temperature before they were filtered off and titrated

Determination No 8 was carried out with 0 010084 N FeCl₃ and the result shows
that, by using 0 01 N FeCl₃ solution, as small a quantity of TiO₂ as 0 002 g may be
accurately determined in the presence of a large excess of iron It might, however,
be preferable to use the Weller colorimetric method in the case of such small quantities
of titanium   All of the other titrations were performed with 0 05042 N FeCl₃ solution

[3] The granulated zinc referred to was 20–30 mesh, "C P " and was used without
amalgamation or further treatment

ores. E. Knecht[1] fuses o.5–1.0 g. of the mineral (e. g., rutile) for 10 minutes with 10 parts by weight of potassium hydroxide, after which he washes the mass into a beaker containing a large excess of hydrochloric acid.

A method far better suited to our purpose was suggested to us by Professor W. A. Noyes.[2] According to this, the finely powdered ore is mixed with 1 part, by weight, of potassium fluoride and 5 or 6 parts of potassium pyrosulfate and fused in a platinum crucible for 15–20 minutes, until effervescence ceases. The cooled mass is then readily dissolved by hydrochloric acid to a clear solution which is ready for reduction.

With solutions prepared in this way, the ferric chloride volumetric method gave the following independent values: 34.63, 34.47, 34.44, and 34.42% of TiO_2 (mean value = 34.49%). The reduction in this case also requires not more than two hours.[3]

The ferric chloride method is thus seen to compare very favorably with the tedious gravimetric method of Gooch, and it is incomparably shorter. Such metals as tin, chromium, vanadium, tungsten, and molybdenum must, however, be absent when the solution is reduced with zinc.

URBANA, ILL.

THE ARSENATES OF LEAD.[4]

BY HERMAN V TARTAR AND R H. ROBINSON.
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Introduction.

Some of the arsenates of lead are widely used at present as stomachic insecticides. The general properties of these compounds seem to specially adapt them for this purpose and for this reason they have been used more extensively in recent years than any other arsenical. In response to the demand for these materials, their commercial manufacture has now reached large proportions and a number of manufacturing chemists in the United States are making them in considerable quantity. This extended use of certain of the arsenates of lead for insecticidal purposes

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[1] Z. angew. Chem., 26, 734-5 (1913). Knecht dilutes the HCl solution to 250 cc. and reduces a 25 cc portion of it with granulated zinc and hydrochloric acid for 10–20 minutes, until the zinc is completely dissolved. He then suspends a zinc rod in the hot solution by means of a platinum wire which is passed through the Bunsen valve, and allows the solution to cool; finally he passes in carbon dioxide and titrates with ferric alum.

[2] J. Anal. Appl. Chem., 5, 39 (1891).

[3] Since in all cases good results were obtained after 2 hours' reduction, that time is to be considered sufficient. While in some cases less time might suffice, it is safer always to allow at least 2 hours for the reduction.

[4] Presented at the Cincinnati meeting of the American Chemical Society, April, 1914.

makes a thorough knowledge of their constitution and properties, as well as analytical methods necessary to the valuation of the same, of considerable practical importance.

In connection with some other investigations on insecticides, a study of the preparation and properties of the different arsenates of lead was begun in this laboratory early in 1913   This study has been continued, as opportunity permitted, up to the present time.   We have now sufficient data from which to draw certain conclusions, which are presented herewith.

Historical.

But little attention was given to the arsenates of lead previous to their use as insecticides. Lead orthoarsenate, $Pb_3(AsO_4)_2$, is reported to have been prepared by Mitscherlich[1] by the use of the reaction of disodium hydrogen arsenate, Na_2HAsO_4, with basic lead acetate, or with neutral lead salts. It is also stated that this substance was prepared by Berzelius[2] by the action of ammonia on lead pyroarsenate, $Pb_2As_2O_7$. The substance obtained was a white amorphous powder.

According to Mitscherlich and Berzelius,[3] lead pyroarsenate is precipitated when lead chloride or lead nitrate react in aqueous solution with arsenic acid; also as a precipitate resulting from the reaction of di-ammonium hydrogen arsenate, di-potassium hydrogen arsenate, or di-sodium hydrogen arsenate with lead nitrate in excess.   It is also stated by the authority cited that Salkowski prepared this substance by the use of the reaction of neutral lead acetate and di-sodium hydrogen arsenate and that it is a white, easily melted, amorphous powder.   On the whole, the work of these early investigators is very imperfect and in some instances contradictory.

Moulton,[4] chemist of the Massachusetts Gypsy Moth Commission, was the first to prepare lead arsenate for use as an insecticide.   For this purpose he used lead acetate and di-sodium arsenate.

The work of Moulton was continued by Smith,[5] who studied the reactions involved and other matters pertaining to manufacture.   "He stated that the ordinary spray material was not a single salt, but a mixture of neutral, $Pb_3(AsO_4)_2$, and acid, $PbHAsO_4$, arsenates, and believed that the relative amount of each depended principally upon the source of the soluble lead salt, although temperature and concentration at the moment of precipitation affected the results; in other words, the acetate

[1] Dammer: "Handbuch der Anorganischen Chemie," Vol. 2, Pt. 2, p. 565.
[2] Ibid.
[3] Ibid., p. 566.
[4] Mass. Board Agr. Report, 41, 282 (1894).
[5] Ibid., 45, 357 (1898).

· of lead has a tendency, other factors being equal, to yield the neutral salt and the nitrate the acid salt."[1]

Smith also states that the specific gravity of arsenate of lead is 1.00668 (salt not specified).

Haywood[2] claims that the reaction between lead acetate and di-sodium arsenate takes place as represented by the following equation:

$$3Pb(C_2H_3O_2)_2 + 2Na_2HAsO_4 \longrightarrow Pb_3(AsO_4)_2 + 4NaC_2H_3O_2 + 2CH_3COOH$$
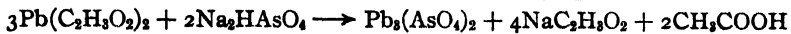
He also found that the reaction between lead nitrate and di-sodium arsenate takes place in the main as follows:

$$Pb(NO_3)_2 + Na_2HAsO_4 \longrightarrow PbHAsO_4 + 2NaNO_3$$

The slight variation in the resulting compound from the theoretical composition of lead hydrogen arsenate caused Haywood to suggest that some unknown secondary reaction took place to small extent.

Haywood and McDonnell[3] state that, when pure lead nitrate and di-sodium arsenate are used, the reaction represented by the second equation given in the preceding paragraph proceeds almost according to theory, though a small amount of lead orthoarsenate is usually formed. They also hold that when lead acetate is used a product is obtained at times which is principally lead hydrogen arsenate. They corroborate Smith's[4] statement that the reaction is affected by various conditions, such as concentration, temperature, etc.

Volck[5] devised a quanitative method for the detection of lead hydrogen arsenate in the presence of the lead orthoarsenate. He also proposed the preparation of the orthoarsenate by the use of the reaction of lead hydrogen arsenate with ammonium hydroxide, although he admitted that the samples prepared in this manner contained somewhat less than the theoretical percentage of arsenic oxide. From his experiments, Volck further concluded that the lead hydrogen arsenate hydrolyzes easily to form the orthoarsenate, and that commercial lead arsenate might contain pyroarsenate as a component.

Holland and Reed[6] state that they prepared the orthoarsenate by precipitation, under certain conditions, from dilute solutions of lead acetate and di-sodium arsenate. In proof of this they showed that the amounts of lead and arsenic found in the precipitates corresponded closely to the theoretical composition of the lead salt. These investigators also state that lead hydrogen arsenate "is readily prepared from nitrate of lead and di-sodium hydrogen arsenate, provided dilute solutions are employed

[1] Holland and Reed, Twenty-fourth Ann. Report Mass. Agr Exp Sta.

[2] *Bull.* **105,** Bur. of Chem., U. S. Dept. Agr.

[3] *Ibid., Bull.* **131.**

[4] *Loc. cit.*

[5] *Science,* **33,** 868 (1911).

[6] *Loc. cit.*

and the sodium salt is added carefully in excess (10%). By this method of procedure no difficulty was experienced in producing salts of theoretical composition."

Space will not be taken at this time to go into any extensive criticism of the work that has been done; this will be brought in the discussion of the results presented below. Taken as a whole, the literature indicates that there are at least two common lead arsenates, lead hydrogen arsenate and lead orthoarsenate; that these two compounds are the main components present in ordinary commercial lead arsenate; that lead pyro-arsenate may possibly be present in the commercial salts; and that there is very little accurate knowledge of the preparation and the chemical and physical properties of the pure compounds.

Experimental.

The work completed in this laboratory has been done along special lines which a study of the literature and a consideration of the agricultural use of commercial arsenate of lead indicated to be of most immediate value. The specific points studied naturally fall under five different heads: (1) the preparation of lead hydrogen arsenate, (2) the results of attempts to prepare lead orthoarsenate, (3) the preparation of lead pyroarsenate, (4) the specific gravity and solubility of lead hydrogen arsenate and basic lead arsenate, and (5) the quantitative estimation of lead hydrogen arsenate in the presence of the basic arsenate.

(1) Preparation of Lead Hydrogen Arsenate.

The preparation of this substance was first tried by using the reaction between lead nitrate and di-sodium hydrogen arsenate. Both concentrated and dilute solutions were employed, using the reacting equivalents of the different substances and also one or the other in excess. Many attempts were made and, in some instances, the salts obtained approximated the theoretical composition very closely but not within the experimental error of analysis. Our experiments showed that very slight changes of condition affect the nature of the reaction. After much work had been done it was decided that this method could not be used safely to prepare pure lead hydrogen arsenate, as has been claimed by Morse and Reed.[1]

The preparation of this compound was attempted in several other ways and the best results were obtained by using the following method: Fairly pure lead hydrogen arsenate is prepared by use of the reacton between lead nitrate and di-sodium hydrogen arsenate. The precipitate is washed quite thoroughly with distilled water and then dissolved completely in nitric acid, using just enough of the acid to effect solution. To this solution dilute ammonium hydroxide is added slowly with constant stirring

[1] *Loc. cit.*

until approximately three-fourths of the nitric acid used has been neutralized. During the addition of the ammonium hydroxide the lead hydrogen arsenate will gradually be precipitated. The precipitate is then allowed to stand over night in contact with the solution (which is acid in reaction due to the presence of considerable amount of nitric acid). The supernatant liquid is then decanted through a filter and the precipitate washed first with distilled water slightly acidulated with nitric acid and then with water which has been recently boiled to remove carbon dioxide, until the washings no longer give a test for nitrates with diphenylamine. The precipitate is then dried at 110°.

The salt obtained in this manner is free from nitrates and ammonium salts. It is pure lead hydrogen arsenate and is a white, amorphous, finely divided, fluffy powder. Analyses made of three samples gave results as follows:

	As as As_2O_5 Per cent	Pb as PbO Per cent	Ratio As_2O_5 to PbO	
Sample No 1	32 99	63 92	1	1 937
Sample No 2	32 98	63 92	1	1 937
Sample No 3	32 88	63 70	1	1 937
Theoretical for $PbHAsO_4$	33 15	64 46	1	1 945

It will be noted that the precentages are somewhat lower than the theoretical for lead hydrogen arsenate. This is due to the presence of a small amount of water that cannot be easily removed. Samples do not lose this water below 200°. Experimental work has not been carried out to the point where the writers are able to state if there is a definite temperature at which this moisture can be removed without changing some of the substance into the form of the pyroarsenate. It will also be noted that the ratio of lead oxide to arsenic oxide is a trifle lower than the theoretical. This is due to the fact that the method for determining lead which is now used by the Association of Official Agricultural Chemists is hardly as accurate as the method used for arsenic; there is a tendency for the results to be slightly low.

(2) Results of Attempts to Prepare Lead Orthoarsenate.

The preparation of this compound was first attempted by the use of the reaction between lead acetate and di-sodium hydrogen arsenate. The results obtained showed that this reaction is easily affected by various conditions such as temperature, concentration, the rate in which the substances are brought together, and the amount of salt used in excess. Evidently, this reaction cannot be used to prepare pure orthoarsenate of lead. The insoluble precipitate obtained from the reaction referred to is really a mixture of two different compounds; this will be brought out in a later portion of this paper.

The preparation of the ortho-compound was further attempted by em-

ploying the reaction between ammonium hydroxide and lead hydrogen arsenate as has been suggested by Volck.[1] The ammonium hydroxide used was freed from carbonate by redistillation from barium hydroxide. It was found that the reaction between ammonium hydroxide and lead hydrogen arsenate is complete after the mixture had been heated gently on a steam bath for three hours and that the reaction is the same whether only a slight or large excess of ammonium hydroxide is used. Four samples of the substance obtained in this manner were carefully washed free from soluble salts and then dried at 110°. The analyses of the samples are as follows:

	Arsenic as As_2O_5. Per cent.	Lead as PbO. Per cent.	Ratio As_2O_5 to PbO.
Sample No. 1...................	23.42	74.72	1 : 3.190
Sample No. 2...................	23.43	74.68	1 : 3.189
Sample No. 3...................	23 42	74.86	1 : 3.196
Sample No. 4...................	23.46	74.61	1 : 3.180
Theoretical for $Pb_3(AsO_4)_2$.......	25.57	74.43	1 : 2.911

These results show that the substance obtained is not a pure ortho-arsenate of lead. It contains more lead and less arsenic than the theoretical figures. At first, the authors thought that perhaps there was a small amount of free lead hydroxide present. To ascertain if this were true, the substance was heated in a drying oven to a temperature somewhat greater than 130°. There was no change in color due to the formation of lead oxide nor was there any loss in weight. Even microscopic examination failed to show the presence of any lead oxide. A sample of freshly prepared lead hydroxide, when heated to a temperature a little above 130°, gradually changed to an orange-yellow color with the formation of lead oxide and there was a gradual decrease in weight from loss of water. These results clearly indicate that there is no uncombined lead hydroxide present in the insoluble material resulting from the reaction of ammonium hydroxide with lead hydrogen arsenate. In fact, the tests which have been tried *show that it is a definite chemical compound, a new basic lead arsenate of which there is no mention in the literature*. The analyses indicate that its composition may be represented closely by the formula $21Pb_3(AsO_4)_2.2Pb(OH)_2.10H_2O$. It is a white, amorphous granular powder; microscopical examination does not show any crystalline structure. There is no loss of water at temperatures below 200°.

A number of attempts have been made to prepare a pure ortho-arsenate of lead. In these experiments all of the reactions which are now used in the manufacture of lead arsenate have been tried in aqueous solution and also in non-aqueous solutions so far as conditions would permit. Other possible reactions have been investigated. Without going into any lengthy discussion of the reactions used, the authors

[1] *Loc. cit*

will state that lead orthoarsenate is not formed under the ordinary aqueous conditions employed in the manufacture of commercial lead arsenate, and that it is not a component of the commercial material as has been formerly supposed. The compound present, which has been represented to be the orthoarsenate, is in reality the basic lead arsenate mentioned above. Further proof of this will be brought out in a later portion of this paper.

(3) The Preparation of Lead Pyroarsenate.

Since the presence of this substance in the ordinary commercial salts used for insecticidal purposes has been suggested, it was deemed advisable to undertake the preparation of the pure compound. It would seem, on theoretical grounds, that the simplest method would be by the removal of water by means of heat from lead hydrogen arsenate.

$$2PbHAsO_4 \longrightarrow Pb_2As_2O_7 + H_2O.$$
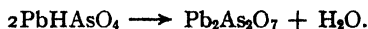
Samples of lead hydrogen arsenate were heated in a drying oven to a temperature somewhat higher than $200°$ without loss in weight. When this compound is fused at a dull red heat, however, it loses water and a white, glassy, somewhat crystalline substance is left on cooling. Analyses made of this substance show it to be the pyroarsenate.

It is well known that pyroarsenic acid does not exist in the presence of water, and consequently if lead pyroarsenate is a constituent of the ordinary commercial salts it must be due to the easy dehydration of lead hydrogen arsenate. The results given above show that this substance has to be heated to a fairly high temperature before loss of water occurs and, evidently, lead pyroarsenate is not a constituent of the commercial lead arsenate.

(4) Specific Gravity and Solubility of Lead Hydrogen Arsenate and Basic Lead Arsenate.

These properties are of much more importance in the consideration of the adaptability of arsenic containing compounds for use as insecticides. A very small amount of soluble arsenic compound ,is sufficient to cause injury to the foliage of fruit trees. Further, an insecticide should be in a fine state of sub-division and of a specific gravity sufficiently low that it will remain in suspension in water for some length of time.

The specific gravity of lead hydrogen arsenate and basic lead arsenate, as prepared by the above described methods, was found by determining the weight of toluene displaced by a known quantity of the salt. The toluene was first dried by means of solid sodium hydroxide and then distilled. Its specific gravity at $20°$ referred to water at $4°$ was found to be 0.8669. Care was taken to remove air from the arsenate when covered with toluene by placing the pycnometer in an exhausted desiccator.

(a) LEAD HYDROGEN ARSENATE.

Grams PbHAsO₄.	Grams toluene displaced.	Specific gravity PbHAsO₄ 20°/4°.
11.1070	1.6610	5.79
11.5724	1 6630	5.79
11.3230	1.6968	5.78

Average 5.786

(b) BASIC LEAD ARSENATE.

Grams basic lead arsenate.	Grams toluene displaced.	Specific gravity basic lead arsenate 20°/4°.
14 5770	1 7794	7.10
20 5749	2 5083	7.11

Average 7.105

There are several things to be considered in making a determination of the solubility of lead hydrogen arsenate. Although one of the hydrogens of arsenic acid resembles the hydrogen of strong acids in its dissociating tendency, the other two hydrogens are those of weak acids. Hence perceptible hydrolysis takes place in solutions of this acid, even when the base combined is strong; that of tertiary salts being greatest in extent. It is difficult to predict the influence of this hydrolysis upon lead hydrogen arsenate. There is also the possibility of the formation of more insoluble normal or basic salts. In discussing the solubility of lead hydrogen arsenate Volck[1] states that "the liberation of the arsenic oxide (arsenic acid) from the acid arsenates depends on transposition to the ortho or neutral arsenate under neutral or alkaline conditions." He also infers that a given quantity of lead hydrogen arsenate can be completely changed to the orthoarsenate by bringing it in contact with water and then replacing the supernatent liquid from time to time with fresh water.

The writers have endeavored to verify Volck's statements. The experiments tried, however, show that arsenic acid is not formed in sufficient quantity by hydrolysis at room temperature to give the qualitative tests suggested by Volck nor can the composition of lead hydrogen arsenate be changed to any appreciable extent by bringing it in contact with an excess of pure water and removing the supernatant liquid from time to time, even though the operation be continued for several days. At temperatures near the boiling point there is evidence of only a slight hydrolysis. We feel safe in stating that if there is any hydrolysis of this substance it is slight and can only be determined by the use of refined physico-chemical methods.

Unfortunately, other pressing work in progress in this laboratory has prevented the taking up of a critical study of this hydrolysis. An idea of the solubility of the salt was obtained, however, by determining the

[1] *Loc. cit.*

amount of arsenic in solution when using the provisional method of the Association of Official Agricultural Chemists[1] for the determination of "water-soluble arsenic oxide" in commercial lead arsenate. Eight hundred cc. of the water extract obtained did not contain sufficient arsenic in solution to be quantitatively estimated by making the final titration with 0.02 N iodine solution. This result indicates that lead hydrogen arsenate is a very insoluble substance.

In attempting to make a determination of the solubility of basic lead arsenate one meets with the numerous perplexing difficulties which are common with the basic salts. These difficulties are such as to preclude perhaps the securing of quantitative data by the usual methods. Use was made of the method of the Association of Official Agricultural Chemists referred to in the preceding paragraph for getting an idea of the solubility of this substance. There was not sufficient arsenic present in eight hundred cc. of the water extract to be estimated by titration with 0.02 N iodine. When warm water was used there was no difference in the results obtained. Evidently, this salt is also very insoluble.

(5) The Quantitative Determination of Lead Hydrogen Arsenate in the Presence of the Basic Arsenate.

At the present time there is no method for estimating the amount of lead hydrogen arsenate in commercial arsenate of lead. It was with the object of securing such a method that this phase of the work was undertaken. It has been shown that when lead hydrogen arsenate is treated with ammonium hydroxide (free from CO_2) under ordinary conditions a basic arsenate of lead of constant composition is formed. The amount of arsenic passing into solution from a given quantity of lead hydrogen arsenate has also been found to be constant. Since the basic arsenate may be considered as insoluble from the usual analytical standpoint, lead hydrogen arsenate in mixtures with the basic arsenate can be easily determined by the following described method:

Take a convenient amount of the finely powdered sample (3–10 g.), depending upon the amount of the acid salt present, which has been dried at 100°, and add 200 cc. of a 5% solution of carbon dioxide-free ammonium hydroxide. Allow to digest with occasional shaking for a few hours at room temperature, when the reaction should be complete. The supernatant liquid is then filtered by suction from the insoluble basic salt by using a Buchner funnel prepared with a pad made of two sheets of filter paper with a layer of asbestos between. The upper paper should be a hardened filter. The filter is finally washed thoroughly with recently boiled distilled water until free from soluble salts. The final washings may be tested with lead nitrate solution to ascertain the completeness of

[1] *Bull.* 107 (Revised), Bur. of Chem., U. S. Dept. Agr.

the removal of the ammonium arsenate. The filtrate should be perfectly clear. In case there is difficulty in obtaining a clear solution it may be overcome by refiltering through a Gooch crucible having a thin layer of carbon black on an asbestos pad. The final filtrate obtained is made up to convenient volume and an aliquot taken for the determination of arsenic. After free ammonium hydroxide is removed by boiling, the arsenic is determined by the modified Gooch and Browning method.[1] The amount of arsenic in the total filtrate calculated as As_2O_5 and then multiplied by the factor 7.6034 gives the amount of lead hydrogen arsenate present in the original mixture.

This method has been tried out on a number of mixtures of known composition and in each case has given good results.

The nature of the insoluble salts formed by the reaction of lead acetate and lead nitrate with di-sodium hydrogen arsenate has been studied in a limited way by using the above described method in conjunction with the usual analytical methods employed. The results obtained are given in Table I:

TABLE I.—THE COMPOSITION OF PRECIPITATES OBTAINED BY REACTIONS OF LEAD ACETATE AND LEAD NITRATE WITH DI-SODIUM HYDROGEN ARSENATE.

Material.	Total lead as PbO. Per cent.	Total arsenic as As_2O_5. Per cent.	Total $PbHAsO_4$. Per cent.	Ratio of As_2O_5 other than that combined as $PbHAsO_4$ to PbO other than that combined as $PbHAsO_4$.
1. Sample prepared by using Pb-$(C_2H_3O_2)_2$ and Na_2HAsO_4 in the theoretical proportion suggested by Haywood......................	73.21	24.93	14.96	1 : 3.189
2. Sample prepared using Na_2HAsO_4 with $Pb(C_2H_3O_2)_2$ in excess......	74.10	24.28	7.42	1 : 3.179
3. Sample made using $Pb(C_2H_3O_2)_2$ with Na_2HAsO_4 in excess..... ...	72.96	24.72	10.48	1 : 3.12
4. Sample made using Na_2HAsO_4 with $Pb(NO_3)_2$ in excess..........	64.73	32.26	93.16	1 : 3.30

These results show that the precipitates obtained were, in each instance, mixtures containing various amounts of the acid salt. It will be noted also that the ratio of the As_2O_5, other than that combined as $PbHAsO_4$, to the PbO, other than that combined as $PbHAsO_4$, approximates within experimental error that found in the basic arsenate already described. These results, considered with the work which has already been presented, seem to leave little doubt that the substance present other than lead hydrogen arsenate is the basic arsenate of lead.

The application of the work here presented to the valuation of commercial samples of lead arsenate will be presented at an early date for publication in the *Journal of Industrial and Engineering Chemistry.*

[1] *Bull.* 107 (Revised), Bur. of Chem., U. S. Dept. Agr.

Summary.

1. A reliable method has been devised for the preparation of pure lead hydrogen arsenate.

2. All attempts to prepare pure lead orthoarsenate have been unsuccessful.

3. Lead pyroarsenate has been prepared.

4. A new basic lead arsenate of apparently constant composition has been obtained.

5. The specific gravity of lead hydrogen arsenate and basic lead arsenate have been determined.

6. The difficulties attending the accurate determination of ,the solubility of the compounds prepared have been pointed out. The tests made, however, show these substances to be relatively insoluble.

7. A quantitative method has been devised for the estimation of lead hydrogen arsenate in mixtures of this substance with the basic arsenate.

8. The results show that the precipitates obtained from the reactions of lead acetate and lead nitrate with di-sodium hydrogen arsenate under certain conditions are mixtures of lead hydrogen arsenate and the basic lead arsenate.

CORVALLIS, OREGON.

THORIUM AMMONIUM OXALATE.

BY C. JAMES, C. F. WHITTEMORE AND H. C. HOLDEN.
Received June 4, 1914.

Bahr[1] found that thorium oxalate dissolved in a warm solution of ammonium oxalate, and Bunsen[2] showed that this reaction might be employed for separating thorium from the rare earths.

Brauner[3] investigated the subject more thoroughly and showed that, when thorium oxalate was dissolved by ammonium oxalate, a definite ammonium thoroxalate was formed, to which he ascribed the formula $Th(C_2O_4.NH_4)_4.7H_2O$. This hydrate was said to separate from a supersaturated solution, while a lower hydrate possessing four molecules of water was obtained by spontaneous evaporation. When the ammonium thoroxalate was treated with water, it was hydrolyzed. The resulting product was very colloidal and passed through filter paper. It required two months time in order to settle. Later, however, a precipitate was obtained that became crystalline. These crystals possessed the formula $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.7H_2O$.

The writers decided that a study of the solubility curves of thorium

[1] *Ann.*, **132**, 231.

[2] *Ann. Phys. Chem.*, **155**, 375.

[3] *J. Chem. Soc.*, **73**, 951.

oxalate and ammonium oxalate, in the presence of each other in water, would show clearly and distinctly the number and kinds of compounds existing. This work was commenced in 1912, and it appears O. Hauser started work along similar lines at a similar date.[1]

In order to determine the various solubilities, several bottles were prepared and placed in a thermostat at 25°. They contained varying amounts of thorium oxalate and ammonium oxalate with sufficient water to make 50 cc. After rotating for many weeks, the bottles were allowed to stand at the same temperature until the supernatant liquid became clear, when portions were withdrawn for analysis. In each of the samples, thorium oxide and C_2O_3 were determined. The thorium content was obtained by evaporating a weighed portion of the solution in a tared platinum dish, and igniting the residue to oxide. The C_2O_3 was found by titrating with a standard potassium permanganate solution.
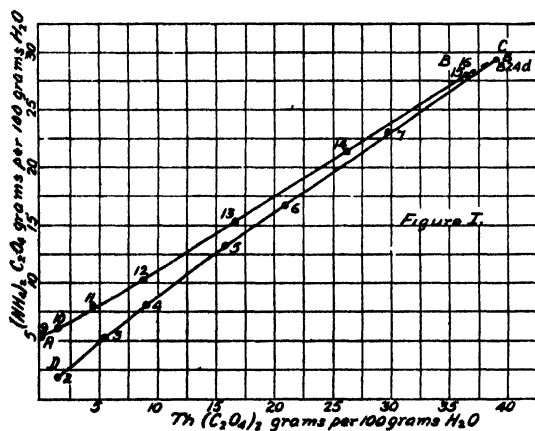
Figure I.

The results are given in Table I, and plotted in Fig. 1.

The data when plotted are not quite sufficient to complete the curve. No points were obtained between B and C, which are evidently transition points. Later, it was found that the solid phase, in the bottles from 2 to 8 along that portion of the curve CD, consisted of a definite compound. It, therefore, became necessary to follow the curve more completely between the points B and C and from bottle 2 to the zero point. More bottles were, therefore, pre-

Figure II.
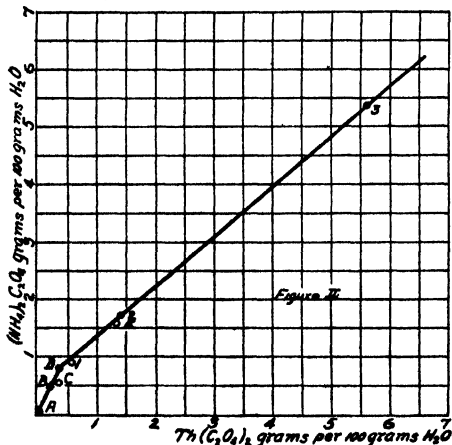
[1] R. J. Meyer und O. Hauser, "Analyse der seltenen Erden und Erdsäuren," p. 167.

pared and rotated for several months in a thermostat at 25°. It was necessary to rotate for a considerable length of time; otherwise, results of a metastable condition would be obtained. The data are given in Table II and plotted in Fig. 2.

TABLE I.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.	G. $(NH_4)_2C_2O_4$ per 100 g. H_2O	G. $Th(C_2O_4)_2$ per 100 g. H_2O.
1	0.89	0.57	0.90	0.58
2	1.65	1.38	1.70	1.42
3	4.83	5.06	5.36	5.63
4	6.93	7.79	8.13	9.13
5	10.27	12.35	13.27	15.96
6	12.20	15.35	16.84	21.18
7	15.07	19.54	23.04	29.87
8	17.49	23.19	29.47	39.10
9	4.98	...	5.25	...
10	5.62	1.43	6.04	1.54
11	6.93	4.07	7.78	4.51
12	8.70	7.40	10.37	8.82
13(a)	11.68	12.76	15.46	16.89
13(b)	11.68	12.77	...	...
14	14.52	17.84	21.47	26.37
15	17.11	22.18	28.18	36.54
16	17.13	22.16	28.21	36.51
8(s)	17.49	23.19	...	...
4(d)	Results of analysis identical with those of 8(s)			

TABLE II.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.	G. $(NH_4)_2C_2O_4$ per 100 g. H_2O	G. $Th(C_2O_4)_2$ per 100 g. H_2O.
A	0.03	0.03	0.03	0.03
B	0.48	0.20	0.48	0.20
C	0.52	0.36	0.52	0.36
D	0.79	0.35	0.80	0.35
E	1.50	1.31	1.54	1.35

Points 1, 2 and 3 are taken from Table I, and are the same as in Fig. 1.

TABLE III.

Solid Phase.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.
2	10.51	66.39
3	10.84	64.77
5	12.78	63.98
6	12.65	63.87
7	13.40	66.42
A	0.00	66.89
B	3.17	64.85

Unfortunately, no new points came between B and C. Samples of the solid phase, along that part of the curve from C in Fig. 1 to A in Fig. 2, were withdrawn by means of a platinum spoon, and freed as much as pos-

sible from the mother liquor by pressing between filter papers in a screw press. The pressed sample was quickly transferred to a weighing bottle and thoroughly mixed.
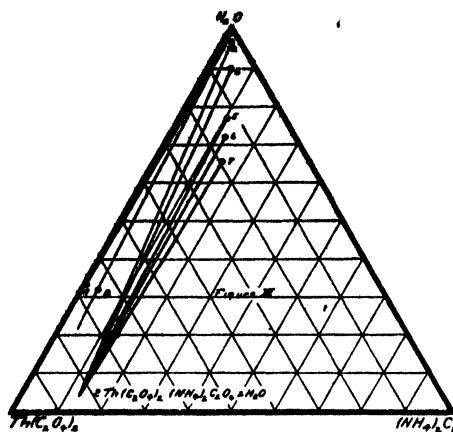
The thorium oxide and C_2O_3 contents were then determined.

The data are given in Table III and plotted in Fig.3.

It will be seen that lines joining the points of the corresponding liquid and solid phases meet at a common point, expressed by the formula $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.2H_2O$. This does not entirely agree with the results obtained by O. Hauser, since he finds three molecules of water present. However, the authors give the formula as obtained by the triangular diagram, and not from the analysis of the pure compound.

That portion of the curve in Fig. 1 represented by the line AB shows the solubility of thorium oxalate in ammonium oxalate. B and C are evidently transition points and the solid phase occurring in any bottles coming between these points should consist of the normal compound, $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.7H_2O$, as described by Brauner. From point C in Fig. 1 to point D in Fig. 2, there exists, as the solid phase, the compound shown in the triangular diagram. From D to A in Fig. 2, the solid phase consists of thorium oxalate. Lines joining the corresponding points, representing the liquid and solid phases, do not meet.

This work indicates that at $25°$ there are only two ammonium thoroxalates.

DURHAM, N H

THERMOELEMENT INSTALLATIONS, ESPECIALLY FOR CALORIMETRY.

BY WALTER P WHITE

For maximum precision in calorimetry, electrical thermometers are essential, and they are often considered to be also the most convenient. Among them the least exacting, the most accurate for small intervals, and the freest from sources of error is the multiple thermoelement when used with a small temperature difference between its two ends. With it the relative precision required in the electrical measurement is ordinarily

from a hundredth to a thousandth of that needed with the resistance thermometer for the same thermometric precision. It is, accordingly, sometimes nearly indispensable, often the most convenient, and very seldom appreciably less advantageous than other types.

The thermoelement has been employed in this way for a number of years in calorimetric methods of great delicacy though of somewhat restricted scope, but the newer and more widely applicable thermoelement technic has scarcely been used in chemical work as yet, and appears accordingly to be rather unfamiliar to chemists. It has therefore seemed best, in presenting some recent modifications, to attempt also a rather complete account of the thermoelectric procedure, beginning in the present paper with the fundamental methods and apparatus, and following with descriptions of the thermoelement and of its application to the calorimeter. The methods and arrangements to be described are also in large part advantageous for precision thermoelement work in other subjects besides calorimetry.

1. The Thermoelectric Methods in General.

The salient features of the thermoelectric methods here presented are: (a) The temperature to be measured acts on the thermoelement, which is simply a slender, flexible bundle of fine, insulated wires, easily enclosed in a variety of ways, and, when once enclosed, detrimentally affected only by very severe treatment. No heat is produced in it. (b) The electrical quantity (electromotive force) furnished by this thermoelement is about proportional to the temperature interval, and, therefore, the relative precision required for measuring it is extraordinarily low, as already mentioned. (c) The electromotive force is measured with a potentiometer. (d) The system shares the general advantage of all potential methods, namely, it possesses an almost complete indifference to contact resistance, and thereby avoids one of the most troublesome and insidious sources of error in electrical work. (e) One consequence of this property is that the reading of different temperatures or electrical quantities during the same experiment is especially easy with the thermoelectric installation. (f) The thermoelement measures, primarily, only differences of temperature, hence some body of definite thermal condition must be provided to control the end not in the calorimeter. This provision, though it affords the means of simplifying the electrical measurement (as already pointed out), is also an inconvenience.

2. The Relative Precision Required.

The coils of the potentiometer must, in the nature of things, evidently be *calibrated* with as great relative precision as is to be obtained in the temperature determinations. This of course applies only to the coils of the highest valued decade used in any particular determination.

Potentiometer coils are ordinarily *adjusted* with a precision of from 1 per mille to 0.1 per mille. Hence corrections to the higher valued coils will often be necessary in working to 0.1 per mille, but will disappear entirely when the precision is less, or the instrument is very well adjusted. These corrections will be small and invariable; no coil corrections for temperature will ever be needed.

If the standard cell by which the potentiometer is regulated is a saturated cadmium cell, its electromotive force will vary 0.0001 for every $2°$ change in temperature, and a small temperature correction may be needed in very accurate work. The temperature correction of a Weston cell will be quite negligible.

The corrections required are therefore less than are usual with either a mercury thermometer or an electrical resistance thermometer.

3. The Absolute Precision Required.

The absolute precision required is the subject of most of the misconception which may exist regarding the thermoelectric system. Much potentiometer work is of such a character that for it a precision of 10 microvolts is remarkably good. With respect to this work, and to the corresponding apparatus, methods, and habits of thought, the precision of one-tenth of a microvolt, here recommended for thermoelectric work, is apt to appear extreme. The truth is, however, that this degree of precision has been selected not because it is indispensable, but because it has been found to be easily attainable in daily work, under any but the worst conditions.

A thermoelement of 24 copper-constantan couples, which may be only 5 mm. in diameter when enclosed, and will then seldom have more than 120 ohms resistance, is easily made and very convenient, and may be taken as the standard size for calorimetry. With it an *electrical* precision of 0.1 microvolt means a *thermometric* precision of $0.0001°$. An electrical precision of 0.1 microvolt, therefore, is better than will usually be required for calorimetry, though 1.0 microvolt will be required in any case where the precision of electrical methods is needed at all. In *high temperature work* with platinum thermoelements a microvolt is usually the smallest quantity read, but it is sometimes very desirable in laboratory work at high temperatures to be able to read closer. In what follows here the precision in view will be 0.1 microvolt, as being easily attainable and often desirable or necessary. This precision, although greater than that used in some kinds of potentiometer work, is really low considering the thermometric precision obtained with it; it is only about half the microvolt precision commonly used to get a thermometric precision of $0.0001°$ with some of the best resistance thermometers.

4. The Instrumental Arrangements Needed to Give the Desirable Absolute Precision.

A precision of 0.1 microvolt, even though it is easily maintained, will of course require apparatus of greater effectiveness than is needed for reading to 10 microvolts. The galvanometer must evidently be more sensitive, though the sensitiveness needed is not extreme.

Secondly, the potentiometer, though it may be simpler and less expensive than the types most commonly used to-day, must be different from them, having greater precision, though its range may be less.

Finally, there must be one feature which is not found at all in potentiometer systems devoted to coarser measurements, but which is found in some form in Wheatstone bridges and other electrical installations of high precision; this is an arrangement for eliminating the effect of parasitic electromotive forces due to slight irregularities of temperature in various parts of the galvanometer circuit. Attempts have been made to avoid these in thermoelectric work by substituting copper for other metals at a few points in the galvanometer circuit and taking great care as to the room temperature, but such a procedure is laborious, and a vain thing for safety. The effect of the parasitics, however, can be eliminated from nearly all the circuit with ease and certainty by a suitable eliminating switch.

5. The Eliminating Switch.

The essentials in the operation of one form of eliminating switch are: (a) To remove from the galvanometer circuit the main electromotive forces, namely, those of the battery and of the thermoelement, leaving the parasitics alone in the circuit; (b) to eliminate the deflection due to the parasitics by moving the telescope or scale (by a "slow motion" of course) so that the galvanometer reading is zero; (c) to return the principal electromotive forces and read directly the *additional* deflection produced by them.

An admirable instrument for making this adjustment is a common
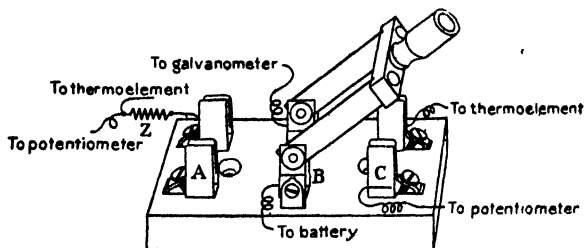
Fig 1.—Knife switch arranged to eliminate parasitic electromotive forces.

2-way, 2-pole copper knife switch. Fig. 1 shows the method of connection. In the figure the knives are thrown to the left for the adjustment

and to the right for the reading. Z is a resistance, to be explained presently.

The simple connections required can, of course, be secured in numberless ways,[1] but for low cost, minimum of attention required, and minimum probability of accident or trouble in working, there appears to be nothing equal to the knife switch.

The convenience of the knife switch can also be still further increased if the ordinary knife is replaced by one of twice the length, whose two ends make an obtuse angle with each other, as in Fig. 9 of the following paper in this series. The throw of the switch then requires a much shorter and simpler motion, and can be made by means of a pull rod, as in Fig. 9. From this latter fact follow several advantages: the switches can be protected by a box, through whose side the pull rods pass; a number of switches can be worked from almost the same point, immediately under the operator's hand; and the motion of several switches can be made nearly or quite simultaneous.   This is an especial advantage in potentiometer work; illustrations of it will be given in Figs. 8 and 11 of the following paper. Switches of this modified pattern can be obtained from the manufacturers at about 40 cents extra cost each, for small orders.

In throwing the eliminating switch, it is essential that the thermoelement circuit should open before the battery circuit, and close after it, or else there may be a very large galvanometer deflection which would generally spoil the adjustment.   This requirement is easily met by filing off a little from the edge of the knife on the thermoelement side of the switch.

The opening of the battery circuit when the switch is thrown removes the corresponding electromotive force without materially changing the galvanometer circuit, but the electromotive force of the thermoelement cannot be removed without disconnecting the thermoelement itself. But the deflection due to the parasitics will not remain the same unless the resistance of the circuit is the same.   Hence during the adjustment a coil must be inserted, approximately equal in resistance to the missing thermoelement.   This is Z of Fig. 1.   If the maximum parasitic force is 4 microvolts (a rather large value) and the precision is to be to 0.1 microvolt, the parasitic currents evidently must not be changed as much as one-fortieth in the adjustment, and the galvanometer circuit resistance must therefore remain as constant as that.   A constancy of 1% in the resistance is twice what is needed, and so gives a satisfactory margin of safety.   Hence it will be sufficient if the resistance of the thermoelement does not differ from that of the coil Z, by more than 1% of the resistance of the whole circuit, that is, by more than from 2 to 10 ohms, as the case

[1] See, for instance, "Potentiometer Installation, Especially for Thermoelectric and High Temperature Work." *Phys. Rev.*, **25**, 344 (1907).

may be. This degree of equality is, of course, very easily secured, and the necessity for it is in any case no objection to this method of elimination, since it is also usually desirable in order to maintain proper galvanometer sensitiveness[1] where several thermoelements are in use. The thermo-elements with their leads must then be made equal to each other in resistance, and hence might as well also be made equal to Z.

There are several other effective methods of eliminating the effects of the parasitic forces, but the one just described appears on the whole to be preferable, at any rate for precision not very much greater than o.1 microvolt.[2]

6. "Neutral" Contacts and Connections.

The arrangement and procedure just described effectively eliminate parasitic troubles in the galvanometer and the potentiometer; it is also necessary that the switch itself, and the leads from it to the thermoele-

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[1] For reading to *one-hundredth* microvolt with a 4 microvolt parasitic force, a constancy of resistance to about o.oo1 of the total would be desirable, and to maintain this with various thermoelements might be troublesome, particularly if the total resistance had to be low, in order to gain sufficient sensitiveness. Hence in such a case there is more reason for preferring one of the methods of elimination, described in the following foot-note, which dispenses with the resistance Z. But it should be noted that to attempt to eliminate any parasitic effect to 1/400 of its value is a very unpromising task, so that readings to o.o1 microvolt will generally be accompanied by precautions against the occurrence of any parasitics approaching 4 microvolts in value, and in that case the resistance adjustment might still be preferable.

[2] (a) It is possible to record and apply a correction instead of adjusting the scale, but this is more laborious, complicates the record, and unless one is very systematic about it, may be a source of mistake. The correction must be applied to every accurate reading, while the adjustment, once made, is good for from one to ten minutes. (b) Instead of the deflection produced, the electromotive force itself may be compensated, by means of a device which is really a little potentiometer, made of a battery, a high resistance, and a very small variable resistance (A. D. Palmer, *Phys. Rev.*, **21**, 72 (1905), and several other writers). This method, however, is not valid unless either (1) the resistance is kept constant, or (2) the galvanometer is first made to read zero on open circuit. But (1) with resistance adjusted to be constant this method is more complicated with the movable scale, without any countervailing advantage, while (2) in the other case it requires two adjustments, of which the one on open circuit is very tedious with moving coil galvanometers. The method, however, might still be worth while in very delicate measurements, especially if, as is likely to occur with them, the galvanometer was of the Broca type, which is damped on open circuit. (c) Another method of eliminating the effect of the parasitics is to reverse simultaneously both the battery and the thermoelement, by means of two commutators operated together, when half the algebraic sum of the two deflections obtained is the true deflection. Here the resistance is bound to be constant without any special arrangements, but this, as has been stated, is practically no advantage for precision not greater than to o.1 microvolt, since constant resistance is needed also to give constant galvanometer sensitiveness; on the other hand, the method carries to an even greater degree the complexities of record and other defects which result from recording the zero reading, and this disadvantage, it is evident, is especially great in reading varying electromotive forces.

ment, be "*neutral*," that is, free from parasitic thermal electromotive forces. Thermoelectromotive forces are necessarily absent where no temperature difference exists, a condition which is often secured in switches by immersing them wholly in oil. This troublesome precaution, however, is quite unnecessary in working to 0.1 microvolt. Both the switch and the thermoelement leads can very easily be made sufficiently neutral, under all temperature conditions ordinarily occurring, by taking advantage of the uniformity and homogeneity now characteristic of the ordinary commercial copper sold for electrical purposes.[1]

There is, first, no danger of trouble along any single uninterrupted length of copper wire. Second, the very slight differences in thermoelectric quality which may possibly exist between wire and terminal are rendered harmless by the fact that these may all easily be made to occur in pairs, in each of which the two members are close together (and therefore always at the same temperature), and so connected that the exceedingly minute thermal forces either oppose each other or (in the eliminating switch) are substituted one for the other. And finally, the presence of thermal forces in the contact surfaces can be very easily prevented by appropriate methods of construction. These forces, whose existence is perhaps not universally recognized, are due to the fact that wherever two pieces of the same metal come together, whether soldered or not, the material right at the contact surface is thermoelectrically decidedly different from the rest. As long as the two metals on each side of this thin layer are at the same temperature, no trouble whatever results, but appreciable thermal forces are produced if there is a temperature gradient through the contact layer A very effective way to prevent the formation of such a gradient in a temporary contact is to make the contact occur between two thin flat strips of metal, which will evidently come immediately to a common temperature, if the contact is good. A knife switch is excellent in this respect, but a still more effectively neutral contact is obtained by means of a very thin strip of copper, pulled into a spring clothes-pin, which serves as a clamp to main-

Fig 2.— tain pressure on the contact. Cables or wires terminated by Quick, mov- such contacts (Fig. 2), which are made to grasp other thin able, neutral strips of copper, can be thoroughly recommended for the con-(or "anti-thermoelec- nection between the thermo-element and the eliminating tric") con- switch, being rapid, adaptable, exceedingly cheap, and thermo-tact. electrically unexcelled.

This type of contact, by the way, really has a very wide range of profita-

[1] For data as to this, see "The Thermoelement as a Precision Thermometer," *Phys. Rev*, **31**, 149 (1910).

ble use. I have used them for miscellaneous connections, instead of plugs in resistance boxes, as commutators, etc. (by suitable arrangements of several copper strips), and for several years as regular potentiometer switches. They really excel binding posts for most purposes and plugs for many, both on account of their quickness and because the spring insures that they will not spontaneously become loose, but as switches they are a little less convenient than some other arrangements, and are recommended mainly by their low cost and ease of installation.

Where two pieces of copper are *soldered* together, the same general condition obtains as in a temporary contact; that is, there is a thin intervening layer which must be free from temperature gradient. If one of the members is a wire, the equalizing effect of the broad contact is no longer fully obtained, hence it may be well to bring the two conductors to the same temperature before they reach the contact, which is done by putting them close together with thermal but not electrical contact (Wenner). In the clothes-pin contacts, this means merely folding the flat copper strip together over a part of the wire from which the original insulation has *not* been removed (Fig. 2), or, in the case of a more massive terminal, winding the insulated wire around it and cementing with some electrically insulating varnish, such as shellac.[1] As far as I know, this precaution has not been observed to be necessary except when the terminal is rather massive, and therefore apt to differ considerably in temperature from the air, but it is so very easy to take that it is best employed for high precision, and by all means in the eliminating switch of Fig. 1, which ought to be quite above suspicion.

The elimination of parasitic electromotive forces by means of the eliminating switch is very complete, and is dependent only on the effective neutrality of the switch itself, which should therefore be carefully tested as a prelude to any work of precision. The test is easily and quickly made, after the leads have been soldered to the switch, and before these have been permanently connected to the other apparatus. The leads from the two end clips (Fig. 1) are connected together to one terminal of a galvanometer, the lead from the center post to the other terminal; a difference of temperature is produced between the end clips (by holding one awhile between thumb and finger, for instance); the change of deflection caused by throwing over the switch is then observed.

Tests have been made here on four lots of switches, one of unknown make, the others, catalog numbers 710 and 980 of the Trumbull Electric

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[1] The wires should of course be as fine as is convenient. For the outer connections, where some strength is required, anything not larger than 22 cable (7 strands of 0.25 mm. diameter each) is unobjectionable, though for the stationary *neutral* connections much finer wire (0.2 mm or less) had better be used, since its use entails no inconvenience.

Company.   The contact clips were bent-up copper strips (Fig. 3), a form
perhaps more likely than machined contacts to resemble
the knife in quality of metal.   With one clip heated by hold-
ing an incandescent light against it for several minutes the
first deflection on throw-over was o.5 microvolt, falling in 5
seconds to o.1 microvolt, which lasted somewhat longer.
Other similar tests gave comparable results.

There appears, therefore, no doubt that under reason-
able conditions these switches would never show a permanent
parasitic force approaching o.1 microvolt.   To make cer-
tainty still more certain, however, it seems worth while to
shield from drafts, as can be easily and simply done by an inverted box,
perhaps using pull rods to work the switches, which in that case should
have the longer bent knives mentioned above.

Fig. 3.—Con-
tact clip of Fig.
1, in detail.

The substitute coil Z should of course also be thoroughly neutral.   To
make it so, the ends of the manganin coil are joined to very fine copper
terminals, the junctions are brought as close together as possible and so
wrapped or enclosed as to shield them from uneven temperatures without.

7. The Galvanometer.

The work here in view demands from the galvanometer nothing extraor-
dinary or special.   The period need not be less than 5 seconds; the neces-
sary external resistance will not be more than from 60 to 300 ohms, de-
pending mainly on the thermoelement used; the sensitiveness, for reading
to o.1 microvolt, should be 1 mm. per microvolt at 2 meters distance,
that is, one scale division should correspond to a microvolt, and tenths
should be easily estimated.   Moving coil galvanometers of greater sensi-
tiveness than this are now regularly catalogued, while at least two con-
cerns furnish galvanometers whose efficiency is over twenty times that
just stated.[1]   This prescription, however, supposes a steady support for
the galvanometer.   Vibration of the building may lower the *effective*
sensitiveness to one-fifth of its proper value, and may thus diminish the
number of moving coil instruments available for a precision of o.1 micro-
volt.   But some of them would evidently still suffice, while a less precision
than o.1 microvolt suffices in most cases.   Of course, galvanometer diffi-
culties are not an affair of the thermoelement alone, but affect it rather
less, if anything, than they do the resistance thermometer.[2]

[1] One of these is a moderate-priced instrument of the Cambridge Instrument
Company, with a period of only 2.8 sec., a circuit resistance nearly 300 ohms, and a
sensitiveness of *four* millimeters per microvolt at 1 meter.   (For thermoelectric work
with this instrument the resistance should be increased at the expense of the unneces-
sarily short period or of the sensitiveness, which would usually be excessive.)   The
other is a *special* galvanometer of the Leeds and Northrup Co.

[2] Because the microvolt sensitiveness of the resistance thermometer, as ordinarily
used, is less, and the required galvanometer sensitiveness, therefore, greater than with
the thermoelement.

If the type of galvanometer available more than meets requirements, convenience dictates that some of the extra efficiency, at least, should lie in the direction of high resistance, for this makes the circuit less sensitive to changes of resistance, and hence diminishes the care and attention needed to secure the constant galvanometer sensitiveness which permits rapid observing. Little gain comes from having the sensitiveness much more than sufficient to permit estimating the smallest unit which is to be recorded. A satisfactory combination is: microvolt sensitiveness, o 5 (that is, o 5 mm. at 1 meter—the same as 1 mm. at 2 meters); period 3 to 4 seconds: resistance as high as possible up to 1000 or 1200 ohms. The makers of galvanometers can advise regarding the attainment of the most satisfactory performance in any particular case.[1]

Many galvanometer installations could easily be given higher effective sensitiveness by the use of a more powerful telescope. In most cases, also, the sensitiveness can be nearly doubled simply by putting the scale much farther from the mirror than the telescope is—a device presumably well known, but surprisingly little used.

For high temperature work and in other cases where a precision of only a microvolt is counted sufficient, the galvanometer may be less sensitive, and therefore cheaper and a little less delicate to handle, but in such work high resistance and shortness of period are often more important than in calorimetry.

8. Special Conveniences of the Thermoelement System.

The very simple eliminating switch with its neutral contacts, the fairly sensitive galvanometer, and an appropriate potentiometer (to be considered later)are the three special features *required* by the auxiliary system of the precision thermoelement. That system *offers* two other features which are of great convenience, namely, facility in reading different instruments during the same observation, and facility in using large deflections of the galvanometer so as to simplify observing. Both are possible with other systems, but are especially effective with this. The reading of different instruments is somewhat dependent on the design of the potentiometer, and will be treated along with it in a following paper.

9. Deflection Reading.

One great and largely unappreciated advantage of thermoelement and potentiometer methods is the ease with which switch manipulation can be diminished, and time and errors accordingly saved, by the accurate reading of relatively large galvanometer deflections.

The relations of all-deflection, partial deflection, and null methods, are well illustrated by the case of the balance. An all-deflection instru-

[1] Some help may also be obtained from a rather technical discussion in "Every-Day Problems of the Moving Coil Galvanometer," *Phys. Rev.*, 23, 382 (1906).

ment is the spring balance, quick but relatively inaccurate. The null method, accurate but slow, is obtained when the beam balance is counter-poised till it reads exactly zero. The partial deflection method, inter-mediate in speed, but quite equal to the null in precision, is merely the ordinary practice, where the last figures of the result are read with the pointer. It requires, of course, a moderately constant sensitiveness.

In electrical measurement, the obtaining of an exact balance is usually less tedious than in weighing, and the maintenance of constant galvan-ometer sensitiveness is usually troublesome with the Wheatstone bridge, and also with some potentiometers, hence for electrical work of precision null methods have been extensively used. From this fact, probably, has arisen the tendency, sometimes apparent, to think of null methods as the only possible precision methods in electrical work, which has in one case resulted in the wholly unwarranted assertion that partial deflection methods are intermediate in precision as well as in speed between all deflection and null methods. In reality, partial deflection reading gives quite as much precision in electrical work as null methods do, while with appropriate potentiometers its speed and other advantages are obtained with very little inconvenience.

The partial deflection method here considered, like the best methods of weighing, has the sensitiveness not merely constant, but in some stand-ard unit, so that the last figures of the result are read directly from the scale, and annexed to the switch reading without addition or subtraction. The proper degree of sensitiveness is obtained by proper selection of scale division length and scale distance. Fig. 4 shows a very convenient method of

Fig 4.—Positive scale with zero at the center, for partial deflection reading.

numbering the scale, which makes all the readings positive and yet brings the zero' at the middle. It is obtained by adding 1000 to the negative readings as the scale is numbered.

To maintain constant sensitiveness during any set of observations, it is only necessary to keep the galvanometer circuit resistance constant. The reason why the thermoelement system especially favors deflection reading is because the resistance of most thermoelements never varies much, and because the potentiometer can easily be made to have a con-stant resistance in the galvanometer circuit.[1] The very slight changes in galvanometer sensitiveness due to other causes can be corrected by

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[1] In case it does not have this, a hand regulation of the circuit resistance is easy and well worth while, except where frequent and considerable changes of the potentiom-eter setting are being made. See "Potentiometer Installation," *Loc. cit.*, pp. 337–340.

adjusting the circuit resistance or by varying the scale distance, as may be convenient. The sensitiveness can, of course, be adjusted or verified in a moment at any time, since it can be tested, while any nearly constant electromotive force is being read, by merely moving one of the switches and noting the resulting change of deflection.

Where different thermoelements (or other apparatus in their place) are used, the necessary constancy of resistance is secured by inserting in the circuit with each a small, *neutral*, "complementary" coil, so adjusted that the combined resistance of coil and thermoelement is, to a rough approximation, the same in every case, and equal to the coil Z of the eliminating switch.[1] Since these coils help to secure not only the advantages of deflection reading, but also the most convenient method of eliminating parasitic forces, the very slight labor of making them is well worth while. As a rule, the ease and convenience which recommend this method are destroyed by an attempt to keep the galvanometer sensitiveness certainly constant to 1 per mille. It is therefore generally best to read only the last two figures of the result on the galvanometer, which calls for complementary resistances adjusted to at most 0 5% of the total galvanometer circuit resistance, that is, only to one ohm or more.

The advantages of deflection reading lie in several directions. There is first, in general, the evident gain in convenience and speed, with attendant diminution of the chances for mistakes in recording, and also, incidentally, a reduction, sometimes very important, of the number of switch dials needed in the potentiometer. Second, there are special advantages wherever, as in most thermal work, the electromotive force read is varying.

In such determinations, the only way to work the *null* method is to observe the more or less irregular times at which the scale reading passes through zero for different previous settings of the switches. A chronograph is needed for any considerable precision, and the simultaneous following of two or more differently varying temperatures, often essential and nearly always desirable in melting point and recalescence work, is difficult and confusing. When deflections are read, on the other hand, the observer, watching the scale while he gets the exact instant of reading from the ticking of his timepiece or from a bell signal, easily takes accu-

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[1] It is convenient to make the terminals of these coils consist of two flat copper strips, 3 or 4 cm long, close together and separated by mica or celluloid, which are put in the circuit by being inserted between the line and switch terminals, as these are clamped together. A very compact, convenient, and easily constructed arrangement results if the copper strips are made to hold the coil (laid flat) between them, being held together by bending the edges of one over the other, of course with an insulating strip between They are stamped or marked to indicate with what thermoelements they may be used. The manganin wire of the coils is connected to the terminals by means of fine copper wire, with other precautions as already described for neutral coils in connection with the description of the coil Z.

rately timed readings without the chronograph; frequent readings of differ-ent 'varying temperatures present no difficulties; and the equal timing of the observations greatly facilitates their subsequent treatment.

The latter point is important in calorimetry. As a rule, most of the observations in calorimetry relate to the cooling correction, and are worked up to get the average temperature for a given period of time. For the ir-regularly timed data given by null readings, the best method of reduction is to plot and apply a planimeter. But this graphic treatment, very properly recommended as a great saving of labor by those who have had in view the null method data, is clearly much more trouble than the sim-ple addition which alone is required for the data obtained by deflection reading. The observer, therefore, will very soon be repaid for the slight labor needed to fit his installation for deflection reading.

The summary is combined with that of the following paper.

POTENTIOMETERS FOR THERMOELECTRIC MEASUREMENTS ESPECIALLY IN CALORIMETRY.

By WALTER P. WHITE.

In order to be well adapted for accurate thermoelectric work, a potenti-ometer should show a precision of 0.1 microvolt, because this precision, as a rule, can readily be reached in the connections and galvanometer, and to fall short of it in the potentiometer involves a waste of facilities, limiting by so much the efficiency of the thermoelement. There are also other features which, though not essential, are desirable in a potentiometer for thermoelectric purposes. The range, however, may be relatively low, so that such potentiometers, in spite of their high precision, are of relatively low cost. To avoid confusion it may be well to point out that some slide-wire instruments, specially designated as "thermoelectric," have little in common with the instruments here considered, and are, in fact, peculiarly undeserving of their name on any grounds, having almost no feature which specially adapts them for thermoelectric work, and several which hinder. These potentiometers, however, like most others, are satisfactory in many cases, and particularly in high temperature measurements, where the sensitiveness, and usually the precision also, of the thermoelement, is far in excess of requirements.

1. Essentials of the Potentiometer in General.

A potentiometer is a row of resistances in series, through which a cur-rent, the "auxiliary" current, is passed from a constant battery. This current is kept constant by occasionally adjusting it so that the "drop" (potential difference) through a fixed resistance balances a standard cell. Then, since in a simple circuit the drop is proportional to the resistance,

any desired voltage within the range of the instrument can be obtained by connecting to two points of the circuit, between which lies the appropriate resistance.   This is illustrated in Fig. 1, where P and Q are the points, P O Q the resistance, B the battery.   In the actual instrument, the contacts at P and Q are the movable contacts of dial switches or slide wires.   To measure an unknown electromotive force, the unknown, X, is connected across P and Q, which are then moved so as to adjust P O Q till a galvanometer shows by the absence of any deflection that the unknown is balanced by the voltage drop of P O Q, or else, and preferably, an approximate balance is quickly made, and the outstanding difference at once indicated by the galvanometer deflection.
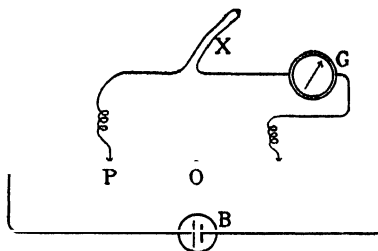
Fig 1 —Potentiometer, simplified. B, battery; P and Q, contacts; G, galvanometer; X, unknown electromotive force to be measured.

The reasons for the superiority of this second, or "partial deflection," method are given in the preceding paper, Section 9; the necessary condition for it is constant sensitiveness of the galvanometer which, in practice, is an affair mainly of constant resistance in the galvanometer circuit. The galvanometer circuit resistance consists, *first*, of the thermoelement, galvanometer connections, and ballast, all of which are practically constant in resistance, and *second*, of the resistance between P and Q in the potentiometer.   In the figure this resistance is the variable resistance P O Q slightly modified by the shunting action of the larger resistance P B Q, but in the best potentiometers the total resultant resistance added to the galvanometer circuit by the potentiometer is, by suitable arrangements, made constant, and therefore is usually quite different from the resistance, P O Q.

2. Features Necessary and Desirable for Thermoelectric Work.

In addition to the obvious and universal requirements of accurate adjustment and adequate insulation, the characteristics desirable in a potentiometer for thermoelectric work are the following:

(*a*) There must be no uncertain resistance (such as a contact resistance) in P O Q. Even a ten-thousandth of an ohm is usually quite inadmissible.

(*b*) The movement of the switches must not change the resistance in series with the battery by as much as 0.00001 of its value, that is, by 0.1 ohm or less, as the case may be.   Such a change evidently produces a proportional effect on the reading.   (In a potentiometer arranged strictly

as in Fig. 1 the motion of the switches can not affect this resistance at all, but in some instruments it may.)

(c) The galvanometer circuit resistance should not be changed as much as 0.5% (that is, as much as one ohm in some cases) by any variation in the resistance P O Q, since such a change restricts the use of deflection reading and therefore hampers work seriously.

(d) The parasitic thermal forces in the galvanometer circuit should be small, and should not be changed by the motion of the switches; that is, the potentiometer should be thermoelectrically *neutral*. This is much less important for the higher-valued dials than for the lower, since the upper dials are not likely to be so often shifted after the adjustment has been made to eliminate the effect of the parasitic forces. If the potentiometer is not neutral the result is an inconvenience in working, but not necessarily any error.

(e) The resistance should not be too low nor too high. A satisfactory resistance is that which makes the battery current 1 milliampere. A current as great as twice this begins to cause too great variability in the voltage of a convenient size of storage battery; a resistance three times as high or more may cut down unduly the galvanometer sensitiveness, but may often be desirable.

3. Types of Potentiometer.

The attainment of these features is complicated by one requirement not indicated in Fig. 1, and that is the need for a greater subdivision of the working range than is given by the two switch dials represented there. It is convenient to classify potentiometers first according to the method of making this provision.

(a) *By Series Coils.*—In one class (Feussner), additional dials are inserted to vary the resistance between P and Q (Fig. 2). This arrangement
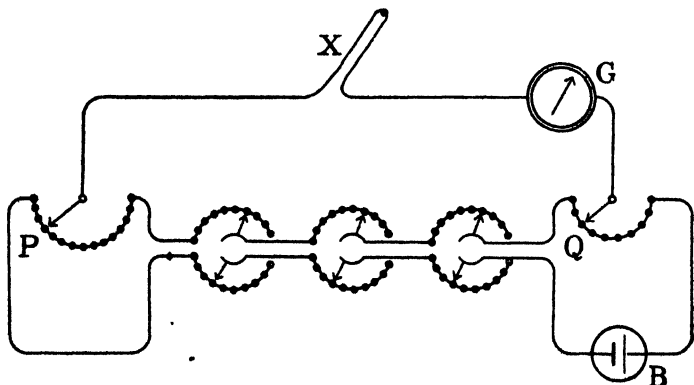
Fig. 2.—General plan of Feussner-Wolff potentiometer.

is not neutral, and, above all, the switch contact introduces too great uncertainty into P O Q. The older Wolff potentiometers are of this kind. Although excellently built instruments, they show, unless well cared for, or with a little exposure to hydrogen sulfide, etc., uncertainties of 10 microvolts or more, corresponding to a switch contact resistance of 0.1 ohm. Well cared for, they are reliable to a microvolt, but for other reasons are not very convenient for thermoelectric work, even with this low degree of precision.

(b) *By Slide Wire.*—In another class of potentiometers one of the contacts represented in Fig. 1 is upon a slide wire, which, with a dial switch for the other contact, gives sufficient subdivision of the range (Fig. 3). These potentiometers are cheap and widely used. Their proper field is the measurement of rather large voltages by null methods. For accurate thermoelectric work they have several disadvantages: (1) The parasitic forces at the sliding contact frequently reach a large fraction of a microvolt, even in the best instruments. (2) Changes of setting take much longer than in all-switch instruments, at any rate where deflection reading is practiced. This often almost precludes using
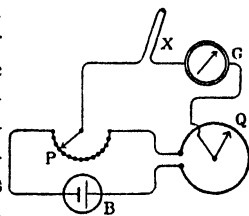
Fig. 3.—General plan of slide wire potentiometer.

the potentiometer to read more than one thermoelement in the same experiment. (3) The galvanometer sensitiveness is necessarily changed by the motion of the switches, unless a ballast resistance is frequently adjusted to correct the variation. (This adjustment is well worth while if necessary to secure deflection reading, but it is better to get the same advantage without it.) Under slightly unfavorable conditions (such as the presence of even a little corroding gas) or in any but the best instruments, the slide-wire contact resistance is so uncertain as to preclude deflection reading altogether.

These potentiometers, though low-priced for their range, are not, absolutely, as cheap as some lower range instruments of higher precision, and there is therefore seldom any reason for preferring them when purchasing an instrument to use with thermoelements of any description. Instruments already in hand, however, if of the newer and better types, may often be successful, if rapidity is not important, and enough thermoelement sensitiveness can be provided to render sufficient a precision of 0.3 microvolt.

(c) *Split Circuit Potentiometers.*—Several types of potentiometer provide additional dials by the device illustrated in Fig. 4. Here the contacts P and Q move on two parallel lines of resistances from points (O and O') originally at the same potential. It is then possible by shunts or external contacts (not shown in Fig. 4) to make changes in the potential of either

P or Q which are additional to and independent of those produced by shifting P or Q, and which do not introduce either contact resistances or thermal forces between P and Q, nor appreciably alter the galvanometer sensitiveness. Three such devices are elsewhere discussed;[1] one of them, that invented by Wenner, can be so arranged that no appreciable error will result from a change in contact resistance as great as 0.0003 of the battery circuit resistance, that is, in many cases as great as 0.4 ohm. All these arrangements require double switches, that is, dial switches making two separate contacts at the same time.

Fig 4 —General plan of split-circuit potentiometer

It appears, then, that in these split circuit potentiometers some of the dials fulfil all the requirements for thermoelectric work enumerated above. For the contacts P and Q so completely satisfactory a result can not be obtained, but a choice must be made between very slight evils, which arise as follows: It is possible to have these contacts in the galvanometer circuit, as in Fig. 1, or else in the battery circuit as in Fig. 5. The switches will of course have to a slight extent both parasitic forces and resistance. If they are in the galvanometer circuit, the battery current will be completely unaffected by them, and their resistance will therefore be of no importance, so that very simple switches can be used, but their slight thermal forces will be effective, and the potentiometer will not be completely neutral unless they are neutral. If the contacts are in the battery circuit, the galvanometer circuit will be quite unaffected and the slight

Fig 5 — Potentiometer with neutrally-arranged ("antithermoelectric") contacts

thermal forces will be swamped by the battery voltage, so that the potentiometer will be neutral, but the contact resistances will affect the battery current, and excellent switches of very low resistance will be needed to keep that sufficiently constant. Either arrangement is satisfactory as a rule; neither the resistance nor the thermal electromotive force of a suitable switch is large enough ordinarily to cause appreciable error in these two dials. For reading to 0.01 microvolt the absolutely neutral arrange-

[1] "Einige Neue Doppelkompensatoren," Walter P. White, *Z. Instr.*, **34**, 111–113, 142–6 (1914).

ment, with switches in the battery circuit, seems preferable; the other is certainly preferable if there is any liability of injury to the contacts from corrosive gases.   It is worth noting, that as to the thermal forces the eliminating switch[1] takes care of them, and also renders it impossible for the observer to be in doubt as to their presence or absence, while errors due to contact *resistance*, on the other hand, are not eliminated or compensated, and are not likely to be even discovered unless specially looked for.   This means, however, not that the potentiometer with interrupted battery circuit has any considerable chance of unsuspected error when properly cared for, but rather that the other is "fool proof" to an unusual degree.   The advantages of both arrangements are substantially secured by putting the contacts in the galvanometer circuit, and making them neutral.[2]   A potentiometer upon this principle is now in use in this laboratory,[2] but is at present not regularly on the market.   Split-circuit potentiometers of the interrupted battery circuit type[3] are made by Wolff of Berlin, according to a design by Diesselhorst.   One of them, a three-dial instrument, can be recommended for thermoelectric work, and is very low in price.

The galvanometer circuit resistance in this Wolff-Diesselhorst instrument is ordinarily about 14 ohms.   It will be advantageous in most cases to order the instrument made with a resistance ten times as great.[4]   In the galvanometer circuit the increase will merely go to displace some of the ballast necessary to make up the desirable 300 to 1000 ohms (see the preceding paper, Section 7), while the battery will be steadier and the possible switch contact resistance error[5] will be diminished.

The slight, easily avoidable, switch contact resistance difficulties encountered in potentiometers such as that just discussed should by no means be confused with those inherent in resistance measurements.   The allowable resistance in a switch of the combination potentiometer, next to be described, is from 3 to 10 ohms; in the Diesselhorst potentiometer it is about 0.01 ohm, raised to about 0.1 ohm by the increase in total resistance just recommended, while with many resistance thermometers it must be as low as 0.00001 ohms, for the same thermometric precision.

The constancy of the galvanometer circuit resistance is not appreciably affected by changes of the contacts P and Q in the Diesselhorst potenti-

[1] Described in the preceding paper, Section 5.

[2] *Z. Instr. (Loc. cit)*, pp. 75–78, 108–113, 149–150.

[3] *Z. Instr.*, **28,** 1 (1908).

[4] This will cause no increase in cost, as Herr Wolff informs me.

[5] The order of magnitude of this error can be found in this particular instrument by noting the change in the auxiliary current (as measured against the standard cadmium cell) which is produced by shifting the switches of the upper two dials.   Those versed in electrical measurements can also easily find the error of the switches by measuring the potential drop through the contacts.

ometer, since these dials are like Fig. 5. In instruments where P and Q are like Fig. 1, auxiliary coils (not shown in Fig. 1) should be added to compensate for the changes produced by moving P or Q, as is done in several of the Geophysical Laboratory potentiometers.[1] These coils do not complicate in any way the single contact switches, and they make the total number of coils the same as in the other type, since in that type similar (but more accurate) coils are needed to keep the *battery* circuit resistance constant.

(*d*) *The Combination Potentiometer.*—A fourth method[2] of adding dials, and one well suited to thermoelectric work, is to connect two otherwise separate[3] potentiometers in the same galvanometer circuit (Fig. 6). Four

dials in all can thus be obtained, which is perhaps the most advantageous number for a low range. The potentiometer giving the two lower dials may, without detriment to the galvanometer sensitiveness, be given a battery circuit resistance of 20,000 ohms or more. These dials may therefore be of the type of Fig. 5 without any danger of uncertain battery circuit resistance, so that the lower dials are far freer from both resistance

Fig. 6.—General plan of 4-dial combination potentiometer. Owing to an oversight, the primes here apply to the *upper* two dials, not the lower, as in Fig. 11.

and thermal e. m. f. troubles than are those of a split-circuit potentiometer. The upper potentiometer may be of either type, just as with the split-circuit instrument, but the more reliable uninterrupted battery circuit arrangement seems best. Two batteries are required, which is an obvious complication. This difficulty, however, as experience has shown, is distinctly of trifling account, and is offset by several advantages, among which are the simplicity and intelligibility of the electrical arrangement, the ability to check the values of the coils at any time by working one potentiometer against the other, and the fact that all the switches are single. The instrument as shown here is also far safer from contact resistance error than any low-range instrument on the market at present. The mechanical and electrical simplicity of this design render it an easy one to get built to order, and thus recommend it where any special features are desired, such as[3] independence of switch contact resistance, or pro-

[1] "Potentiometer Installation," *Loc cit*, p 349; *Z. Instr*, **27**, 216 (1907); **34**, 108–9 (1914) (*Loc cit*)

[2] Suggested but condemned by H Hausrath, *Ann. Phys*, **17**, 740 (1905). Described in *Z Instr*, **34**, 147–148 (1914) (*Loc. cit*).

[3] The two potentiometers, however, easily may be, and preferably should be, balanced by the same standard cell. Of course they may also be in the same box.

vision for the double potentiometer arrangement described in Section 5 below. For a double potentiometer this design has another advantage, since the single switches make it especially suitable for the very inexpensive master switch arrangement described in Section 6.

(e) *Choice of Instrument.*—It follows from the above that there are three potentiometer types which are thoroughly satisfactory for thermoelement work of precision: the split-circuit type with uninterrupted battery circuit (Geophysical Laboratory), the combination potentiometer (Fig. 6) and the Diesselhorst potentiometer when made with tenfold resistance. Of these the first is not regularly manufactured at present. The combination potentiometer, though not yet regularly listed, is easy to procure, on account of its simplicity, and the Diesselhorst is a stock article. Of the two, the combination potentiometer requires a very little more routine manipulation, but requires less care, and is preferable.[1]

4. Special Switch Connections.

(a) When in making the adjustment for eliminating parasitic electromotive forces, the switch of Fig. 1 in the preceding paper is thrown, interrupting the battery current through the potentiometer, it is still often necessary that a battery current of about the same amount should flow somewhere, for unless the current is very small indeed, 0.0003 ampere or less, its discontinuance will generally cause a perceptible variation in the voltage. The necessary substitute current is readily provided by connecting a suitable resistance between the other end of the battery and the clip A in Fig. 1.

A new and better way for low range potentiometers is to connect the clip A to a point between the two potentiometer terminals, so located that the current will still flow much as before through most of the circuit, but will pass around the coils used to balance the unknown, the only ones in which the current needs to be interrupted. To do this the regular connection from the switch runs to the regular potentiometer terminal nearest in potential to the coils in question; and the connection from A runs to a dial contact block just the other side of them. This block thus becomes an "intermediate terminal," I of Figs. 8 and 11. The proper location of each terminal can be found by potential measurements upon the potentiometer top, or by tracing the circuit underneath it.[2] In split-circuit potentiometers the whole split portion must be cut out.

The advantages of the method are that it dispenses with the substitute resistance, and that it avoids at all times the existence in the switch of

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[1] Recent quotations, by an American manufacturer, on single and duplicate combination potentiometers, similar to that in Fig. 11, make that type, as it should be, the lowest priced of the potentiometers here considered (Aug. 14, 1914)

[2] A binding post connected to the intermediate terminal may be provided, but is not necessary.

large potential differences, and thus dispenses with the shielding arrangements often needed to prevent leakage errors due to these potential differences.[1] This advantage holds even where the circuit resistance is so high that interruption of the current causes no unsteadiness, for the danger from leakage increases with the circuit resistance.

(b) Most potentiometers have a key in the galvanometer circuit, often with several associated safety resistances to guard against excessive galvanometer deflections. This combination is with moving coil galvanometers less convenient than the arrangement of Fig. 7, which can be made, at nominal cost, from a couple of single-pole, double-throw switches[2] and three resistances. The resistance of the coil H is 9 times that of the rest of the galvanometer circuit —that is, 9 times that in the potentiometer, thermoelement, and associated resistances—s is 10/81 of H. C is a very high resistance, 100,000 ohms or so, of graphite on glass.

Fig. 7.—Improved galvanometer switches

When the switch A is closed at the back end, the galvanometer is shunted so as to be properly damped for all positions of the switch B. With B open there is no deflection. Closing B at the back end gives a very small deflection, due to current through the safety resistance C. Bringing B forward again closes the circuit without C, giving exactly one-tenth the full sensitiveness. Bringing A forward disconnects S and short-circuits H, giving full sensitiveness. The usual practice will be, in starting an observation, to close B for 1–10 sensitiveness, then set the dial switches, then throw A forward. On opening the circuit both A and B are thrown back together by a single motion. Continuous readings with 1-10 sensitiveness are, of course, often very convenient.

This arrangement is discussed in Z. Instr., **34,** 78–82 (1914), (loc. cit.), where those interested can find further details. It is, of course, a privilege and not a requirement in potentiometer work, and it is therefore, for simplicity, not represented in Figs. 8 and 11 below. If used it would be between the galvanometer and the point marked T.

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[1] These shielding arrangements will be described in a subsequent paper

[2] The single-pole switches with short throw are advantageous They are a regular stock article.

5. Multiple Reading Arrangements.

One virtue of electricity in all its applications is the ease with which its power may be applied by the mere touching of two conductors, and the consequent facility with which different apparatus may be combined, or used in rapid succession. Among measuring devices of precision the potentiometer-thermoelement combination possesses this facility in a high degree, owing to its indifference to contact resistance outside the potentiometer (and often within it); to its adaptability to the partial deflection method, which favors rapid and varied measurements, to the quickness and ease with which equal and interchangeable thermoelements can be constructed; and to the power which the thermoelement has of giving readings with the galvanometer alone. Simultaneous measurements, that is, quickly alternating observations, of the temperature of different bodies or regions are sometimes essential and often recognized to be desirable, and would be found so still more often if convenient means for making them were at hand.

With provision for getting the last two figures of the reading from the galvanometer deflection it will usually be satisfactory to make successive measurements of different temperatures by resetting the switches; there is nearly always ample time for this in calorimetry.[1]

Usually, also, some of the quantities measured are, or can be made to be, small enough to fall within the limits of the galvanometer scale; provision for reading these by the galvanometer deflection alone can be made by a slight addition to the auxiliary switch system, and much resetting of the switches thus avoided.   Fig. 8 shows one arrangement for this purpose,
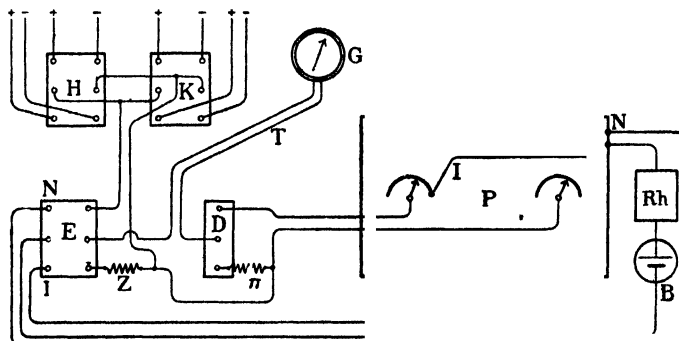
Fig. 8 —Arrangement for combined direct and potentiometer reading of 4 thermoelements. P, potentiometer; I, intermediate terminal; N, negative terminal; Rh, rheostat, B, battery; Z, π, substitute resistances; H, K, thermoelement exchanging switches; E, eliminating switch; D, potentiometer-cut-out, or direct-reading, switch; T, location of galvanometer and cadmium cell switches

[1] This remark may not apply to slide wire instruments.

operated by means of the double-throw knife switch D.   Any one of the thermoelements (here 4 in number) can be instantly connected, either to the potentiometer, or else to the substitute resistance II, which is equal to
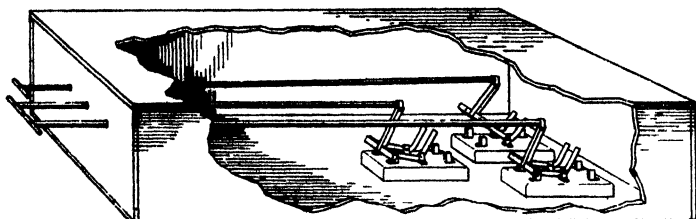
Fig. 9.—Perspective of switches, showing double-ended knives, pull-rod connections, and method of working two switches together

the constant galvanometer circuit resistance in the potentiometer.   E is the eliminating switch of Fig. 1 in the preceding paper, here used with "intermediate" battery circuit connection, I, as described above in Section 4.

Fig 9 shows a construction which favors the rapid operation of the other switches Without it, a resetting may involve three motions. First one thermoelement switch is opened, then the potentiometer-cut-out switch D is thrown across, and then the thermoelement switch is closed on the other side. By grasping at once two of the adjacent handles of Fig. 9, the observer can make this, the most common resetting, in one motion, and never need make but two. The thermoelements which are to be used with the far position of D, that is, with the potentiometer in circuit, are then on the far side of the switches H and K, those to be used with the near position of D are on the near side of H and K. This system avoids the chance of an unusual combination's occurring by mistake, but does not destroy the possibility of making it whenever that becomes desirable. There is, however, surprisingly little danger of confusion, with this or any other system   A habit of moving the switches correctly is formed literally in five or ten minutes

In our switch the pull rods are merely pieces of wooden doweling. They run through guides at the back end also and each is connected to its switch by a pair of connecting rods cut from sheet brass strip. This arrangement works more smoothly and is perhaps a little easier to construct, also, than the one shown, which was chosen for representation as making a more easily intelligible drawing   The handles to the switches are metal bars, slotted so as to fit very tight over the insulating cross bars of the switches and further held by screws. The object of this construction was to make the greatest possible provision against danger of having the handles work loose, which is almost the only way in which this kind of switch can give trouble. If D is to be used with 4 or more switches like H and K, its pull rod is best made of steel for stiffness.

The simultaneous motion of the switches D and H or K is made automatic in our switch in the following way·   D has a shorter handle, so that it is thrown by half the pull-rod motion needed by H or K. On the rod of D are two cross bars, as far apart as the throw of D (or half the throw of H, K, etc.) and so situated as to be pushed by pins passing through the rods of H, K, etc. Then, whenever any of the thermoelement switches H, K, etc., is thrown, it brings D into the right position, leaving the others

of the H, K set in the middle (open) position, and bringing to that open position any thermoelement switch that may have been set on the other side   To make a setting, then, it is only necessary to grasp the handle of the proper thermoelement switch and throw that, when everything else will follow, except in changing from one switch to another on the same side, when two half throws are required   Any unusual combination is readily secured by withdrawing the appropriate pin from its pull rod   It may be well to remark that the less elaborate arrangement shown in the figure is quite satisfactory, but the installation of the more convenient automatic one should not cost an hour's labor, and therefore seems generally worth while

With the scheme of connections shown in Fig 8 the usual direct galvanometer connection to the potentiometer must be omitted during regular readings, but restored for the adjustment against the standard cell   The necessary transfer is easily made by a 3 pole switch, as shown in Fig 10   The switch would be inserted at the point T   The galvanometer terminals of the potentiometer are short circuited by the right-hand knife during regular readings, when the galvanometer is in the circuit at another place

It will often be desirable to read two different and rather large electromotive forces in the same experiment, for which the arrangement just described is of course inadequate.

Resetting of the switches can then usually be facilitated by a simple device   As a rule the observation of two different temperatures will involve making first one setting, then a second, different one, then the first again, then the sec-ond, and so on, with comparatively infrequent changes in either setting. But the time and effort of switch manipulation go mainly not in the mechanical operation of moving the switches, but in thinking *where* to move them and at the same time trying to be sure that no mistake is made. Most of the labor is therefore saved if the
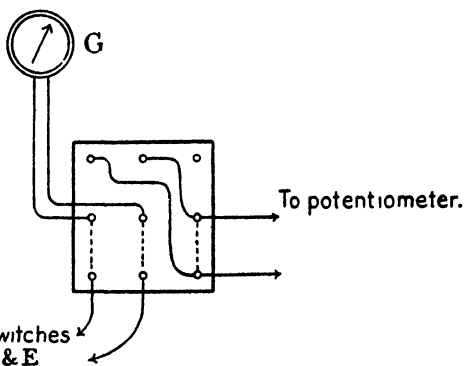
Fig 10 —Switch for making the cadmium cell connection in the arrangement of Fig 8   Inserted at T, Fig 8

two alternate settings are limited by stops against which the switch can be quickly thrown without even looking, and which are shifted from time to time as the settings themselves change.   Very convenient stops can be made of strips of thin hard rubber, which are inserted between the switch blocks.   An indicator appealing to the eye may also be used.   The dial switches are moved after one thermoelement switch is opened, and before the other is closed.   Three or four seconds is ample time for the whole operation.

6. Double Potentiometers.

A more convenient arrangement is to have two sets of switches, and put one or the other into action by a single unvarying motion of a master
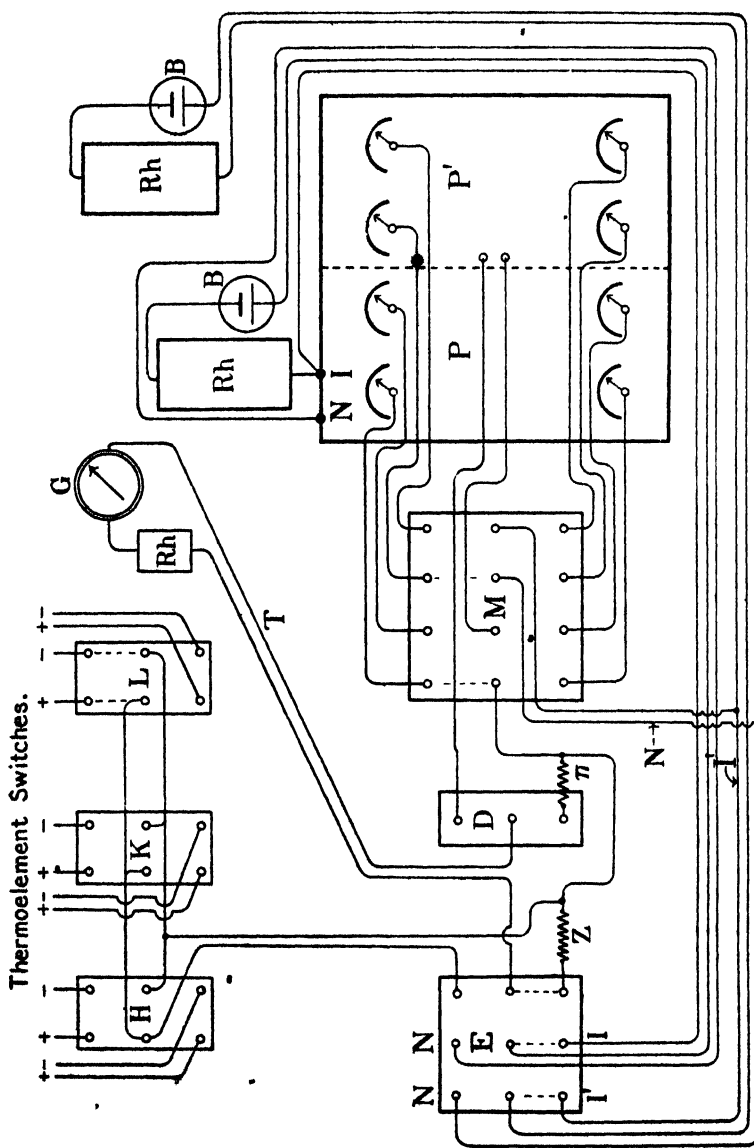
Fig. 11.—Arrangement for making a double potentiometer out of a duplicate dial combination potentiometer. Lettering same as Fig. 8, with M. master switch: P', N' and I' refer to lower half of combination potentiometer.

switch. This gives a *double potentiometer*.[1] It can, of course, be made up as a complete instrument. In that case, especially if a split circuit instrument is the basis, an adequate master switch which is also compact enough is rather expensive, and is preferably avoided by the gridiron construction already referred to.[2] But where extreme compactness and conventional finish are disregarded, as they may be if the observer connects his own apparatus, it is very easy indeed, especially with the combination potentiometer of Section 3 (*d*), above, to arrange a double potentiometer as efficient as the best. The master switch and accessories, made up of various knife switches, are shown as connected to a combination potentiometer in Fig 11   The arrangement for reading by galvanometer deflection alone is also provided here, by means of the single switch in the middle

The eliminating and potentiometer-cut out switches E and D are exactly as in Fig 8, except that E handles 2 batteries, but in place of the simple potentiometer of Fig 8 occurs the master switch M, leading to the combination potentiometer P   M when thrown exchanges the upper dial switches in the galvanometer circuit and the lower dial switches in their battery circuit   The battery circuit of the upper dials and the galvanometer circuit connection to the lower dials remain unaltered   Rh are 3 rheostats for adjusting the two battery circuits and the galvanometer circuit   For simplicity, the intermediate battery circuit terminals I and I' (of Section 4) are located as if most of each battery circuit resistance were in Rh, the exact place of the connection in practice will depend on the arrangement of the particular instrument used   The other connections are exactly as they might be in any case, with a combination potentiometer

The fact that a combination potentiometer is used with two batteries to adjust, of course makes the cadmium standard cell connection somewhat different from that of Fig 10   Fig 12 shows an arrangement calling for 2 ordinary 2-pole, 2-throw knife switches   It is, of course, to be inserted at the point marked   T '   The leads at the right run to fixed resistances such as are frequently used in potentiometers for the standard cell adjustment

This particular arrangement is appropriate to a special instrument, whose galvanometer connection is intended to be made through the switches D, E, and M, with either a key, or a switch like that of Section 4 (*b*) in the circuit near the galvanometer

A simple system for operating the switches D, M, H, K, etc, is to have the thermo-

Fig 12 —Cadmium cell switches for combination potentiometer of Fig 11   Inserted at T

element switches at the right-hand end of the line thrown forward and back in unison with M, according to the method illustrated in Fig 9, and the switches at the left

[1] Described and discussed in *Z Instr*, **34**, 73–78 (1914) (*Loc cit*)   First proposed, *Ibid*, **27**, 218 (1907)   Triple potentiometers are of course possible, but the advantages decrease relatively, and the difficulties increase, as the number of sets of switches increases

[2] *Z Instr*, **34**, 111–142 (*Loc cit*)

similarly thrown forward with D, and also thrown back while D comes forward, using this last, less rapid combination for the least frequent readings.

The arrangement of switches as shown here will be from 20 to 30 cm. wide if "15 ampere" knife switches of stock type are used. Its depth will depend on the number of switches added to those shown here, and therefore on the number of thermoelements provided for. If pull rods are used, as in Fig. 9, a relatively large number of switches can easily be accommodated by putting them beyond those shown in the figure. A considerable extension of the switchboard in the direction away from the operator is not objectionable. There is, therefore, as far as table space is concerned, no difficulty in providing for as many thermoelements as any one is likely to use.

Every essential connection and piece of apparatus has been here indicated. It therefore appears that the advantages of the double potentiometer can be obtained practically at the cost of a few knife switches, for the extra dial switches can be provided at negligible cost in several ways.[1] If a combination potentiometer is made on special order, a duplicate set of regular dials will also cost comparatively little.

The master switch here illustrated is, of course, readily applicable to any potentiometer whose switches do not need to maintain a very low contact resistance, but not as readily to any other. At present no such potentiometer is regularly made which is also suited for thermoelectric work, hence a special instrument, and preferably, for reasons given in Section 4, a combination potentiometer, affords the best means of realizing a double potentiometer. This, however, may be only a temporary situation. Meanwhile, those who need only a single potentiometer will generally find the Diesselhorst type satisfactory; those who need either a double potentiometer or special immunity from contact resistance error can have both, at no great expense, by means of a special instrument of the combination type.

7. The Number of Dials Required.

If the galvanometer deflection is utilized, three dials, with a maximum range of 10,000 microvolts (as in some of the newer Diesselhorst-Wolff potentiometers), are quite sufficient for calorimetry. They permit reading to 0.1 microvolt, and up to a 10° interval with a 24-couple thermoelement. For larger temperature intervals a part of the thermoelement can be used, and though the precision is then less absolutely, it will still be of the order of 1 in 50,000.

For high temperature work, even with a single couple, readings above 10,000 microvolts but below 20,000 are usually needed. They can be provided for with three dials by doubling the current, but the absolute precision is then reduced to 0 2 microvolt. (The double range can be obtained by putting two standard cells, in series, in place of one in an instrument intended for the single range, or it can be provided for in the original construction by the insertion of a suitable coil.)

Voltages above 20,000 are sometimes desirable. A four-coil instrument with range of 100,000 microvolts will provide for them, and with a somewhat lower range

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[1] One method which we have had in use for five years is to screw, to the regular dial contact blocks, tongues of sheet copper 0.5 mm. thick and make contact with these by clamps like Fig. 2 of the previous paper. The relative slowness of this kind of a dial has proved to be but a trifling disadvantage in a *double* potentiometer.

(30,000 to 50,000) and a sufficiently sensitive galvanometer will, at the same time, give an absolute precision in reading of better than 0 1 microvolt, which may be helpful in some cases.

8. Intrinsic Merits of the Thermoelement-Potentiometer Combination.

In view of the amount of detail contained in this and the preceding paper, the cursory reader would scarcely be at fault if he should get the impression that thermoelectric apparatus is elaborate and complicated, and its use beset by pitfalls and precautions. It therefore seems worth while to show, briefly, that the exact opposite is the case. The only essentials peculiar to this system are, as already stated, a galvanometer sensitiveness readily attainable, potentiometer excellences which are admirably embodied in two very low-priced designs, and a common copper knife switch, arranged as an eliminating switch with neutral leads. The amount of detail presented is due, first, to the attempt to give what are practically working directions in a generally unfamiliar subject, and second, to the presentation of arrangements for securing in the observations a rapidity, convenience, and comprehensiveness such as are seldom even thought of in most other systems. The net final effectiveness attained can be fairly well seen by a comparison with the calorimetric resistance thermometer, which has come to be widely recognized as an accurate and convenient instrument.

(a) The *relative* precision required in the electrical measurement is more than a hundred times less with the thermoelement.

(b) The thermoelement is well known to be far less affected by defects of insulation.

(c) Parasitic thermal electromotive forces, the only other noticeable sources of error, require, for their elimination, an arrangement which, though a little more extensive in the case of the thermoelement, is quite as rapid and effective in operation.

(d) The complications and errors arising from the resistance of contacts and leads, so prominent with the resistance thermometer, have been eliminated with the thermoelement.

(e) Very rapid readings and readings made at definite instants of time are more easily secured with the thermoelement system.

(f) The same is true of simultaneous readings of different temperatures, and of concomitant measurements of electrical energy.

(g) The constancy or integrity of the multiple thermoelement can be quickly tested at any time, without interrupting or disturbing any determination that may be in progress. A corresponding test with the resistance thermometer necessitates placing it in a carefully prepared ice bath.

(h) No correction for heat developed, or precautions to avoid undue heat production, are necessary with the thermoelement.

The thermoelement has the disadvantage that some body of definite thermal condition must surround the end not in the calorimeter. This necessity, which will be considered in a later paper, adds visibly to the apparatus required and slightly to the daily manipulation, practically not at all to the chances of error. But on the electrical side the calorimetric thermoelement appears superior in several respects, inferior in none[1] of importance.

Summary of this and the Preceding Article.

These two papers describe a type of auxiliary installation for thermo-elements which in high temperature measurement and other work of moderate precision is valuable for its convenience, quickness, and comprehensiveness, and which is also capable of the very high precision often desired for calorimetry.

(1) When a thermoelement is used with its two ends at nearly the same temperature, a condition easily provided in calorimetry, the *relative* precision required in the electrical measurement falls to a value no greater than that desired in the temperature reading, and the most serious errors ordinarily affecting the electrical thermometer practically disappear.

(2) The *absolute* electrical precision required is also comparatively low. With a convenient and easily made copper-constantan multiple thermo-element of 24 couples, 0.0001° corresponds to 0.1 microvolt.

(3) The satisfactory attainment of a precision of 0.1 microvolt demands two, and only two, special electrical instruments. The first is an arrangement for eliminating the effect of parasitic thermal electromotive forces. A common copper knife switch will perform this service admirably.

(4) The second special requirement is an appropriate potentiometer, that is, one reliable to 0.1 microvolt.

(5) The slide wire and Feussner potentiometers of 1 volt range or more now in common use are not thus reliable, and are otherwise unsuited for thermoelement work. *Split-circuit* potentiometers are satisfactory in this and all other important respects, and so are *combination* potentiometers, or potentiometers having two otherwise separate, very simple instruments in series in the same galvanometer circuit. A very low-priced split-circuit potentiometer is on the market; and the combination potentiometer, on account of its mechanical and electrical simplicity, is an easy instrument to build to order.

(6) The potentiometer system, either with or without the thermo-element, is especially suited to simultaneous measurements of different and differently varying electromotive forces. Its convenience for such measurements can be increased by using a few pieces of hard rubber sheet as stops for the dial switches, and still further increased by arranging a

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[1] This statement and some of the discussion immediately preceding, applies, of course, mainly to the measurement of small temperature intervals, as in calorimetry.

double potentiometer, with duplicate dials.   One effective form of double potentiometer, which employs a master switch, can be arranged at the cost of a few knife switches and very little labor.   An especially suitable instrument to arrange in this way is the combination potentiometer, all of whose dial switches are single, and free from contact resistance error.

(7) Another convenience especially easy to obtain with the thermo-element-potentiometer system is the power to take the last two figures of any reading directly from the galvanometer scale.   It increases speed, simplifies manipulation, diminishes errors, and gives calorimetric data in a form specially convenient for further treatment.

(8) For high temperature measurements and much other thermo-element work not calorimetric, though the required precision may often be less, most of the features above described are desirable, especially the facility for simultaneous and direct readings.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON.

A STUDY OF THE REACTION OF ALKALI SALTS OF SULFONIC ACIDS WITH ALKALI PHENOLATES BY DRY DISTILLATION.

BY EDGAR H. NOLLAU AND LLOYD C. DANIELS.

By analogy to the reaction of alkali sulfonates with alkali hydroxides in the preparation of phenols, aromatic ethers should result from the distillation of sulfonates with phenolates.   Results confirming this idea having been obtained with the simplest mixture of the kind, *viz.*, sodium benzenesulfonate and potassium phenolate, a study of the reaction was undertaken with a view to determining whether it is generally applicable. The trend of the proposed investigation is exhibited by the following mixtures that have been used:

1. Sodium benzenesulfonate and potassium phenolate.
2. Potassium toluenesulfonate and sodium phenolate.
3. Sodium xylenesulfonate and potassium phenolate.
4. Sodium sulfanilate and potassium phenolate.
5. Sodium toluidinesulfonate and potassium phenolate.
6. Sodium α-naphthalenesulfonate and potassium phenolate.
7. Sodium β-naphthalenesulfonate and potassium phenolate.
8. Sodium benzenesulfonate and potassium thymolate.
9. Sodium benzenesulfonate and mono-potassium resorcinate.
10. Sodium benzenesulfonate and di-potassium resorcinate.
11. Sodium methylsulfonate and potassium phenolate.

The problem was to find what radicals might be represented by R

and R' in the following general equation, and what substituent groups might be present in those radicals:

$$RSO_3M + MOR' = ROR' + M_2SO_3$$
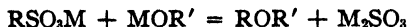
The great variety of possible mixtures made it impossible to cover the whole field, but sufficient has been accomplished to show that the reaction is quite general. But few references could be found in the literature to methods for making aryl ethers of phenols and some of the methods that have been proposed result in rather poor yields. Following is a list of the methods, reference to which was found, with comments on their applicability and on the yields where the latter are stated in the original papers:

I. Action of phenol on diazobenzene sulfate; W. Hoffmeister,[1] yield, very poor. Applicable to the preparation of mixed ethers.

II. Action of anhydrous zinc chloride on phenols; Merz and Weith;[2] yield, usually 6-8%. Not applicable to the preparation of mixed ethers.

III. Distillation of aluminium phenolate; Gladstone and Tribe;[3] yield, about half of the phenolate distilled. Not applicable to the preparation of mixed ethers.

IV. Action of potassium metaphosphate on potassium phenolate (dry distillation); H. von Niederhauesern;[4] yield, less than 1%.

V. Action of phenol on a diazonium salt, phenol used to extract the diazonium salt from solution before the reaction; R. Hirsch;[5] yield, 50% of the aniline used. This is not a good yield considering the large quantity of phenol that must be handled.

VI. Action of halogen substitution products of aromatic hydrocarbons on potassium phenolates in the presence of reduced copper; Ullmann and Sponagel;[6] yields, very high. This method was applied to the preparation of a great variety of ethers and is the source of most of the data on this class of compounds. It is frequently necessary to introduce halogens by way of the corresponding amino compounds, however, and in some cases the corresponding sulfonic acids can be made directly.

VII. One application of the method here proposed was found after this investigation was undertaken. A salt of anthraquinone-α-sulfonic acid was distilled with potassium phenolate, resulting in anthraquinone-α-phenyl ether; R. E. Schmidt;[7] no details given. This same ether has been prepared by patented methods.[8]

[1] Ber., 3, 747 (1869).
[2] Ibid., 14, 187 (1880)
[3] J. Chem. Soc., 41, T5 (1882)
[4] Ber., 15, 1123 (1881).
[5] Ibid., 23, 3705 (1890) and D. R. P. 58,001.
[6] Ann., 350, 83 (1906).
[7] Ber., 37, 94 (1894).
[8] D. R. P. 75,054, 77,818.

The apparatus used in this work was a flat, cylindrical iron retort, 15.5 cm., interior diameter, by 5 cm. depth. The cover of the retort was fastened down with bolts over an asbestos gasket. An iron pipe, 9 mm. in diameter by 50 cm. long, set in the cover with a street elbow, served as the outlet. An Allihn bulb condenser was used, since it was found that the clouds of vapor passed through a Liebig condenser. The apparatus was gas-tight so that distillations could be made at reduced pressure.

Experimental.

Diphenyl Ether, $C_6H_5OC_6H_5$.—An amount of solid potassium hydroxide, equivalent to 30 g. of the anhydrous compound, was dissolved in a small quantity of water and 51 g. of phenol were added to the solution. This phenolate solution and 85 g. of sodium benzenesulfonate were mixed in the retort. After thorough stirring, the mass presented the appearance of a thin white paste. On applying heat, water distilled over and was followed by a brown oil which was caught in a separate receiver. The distillation was continued at increasing temperatures as long as oil was formed.

The total oily portion of the distillate was 44 cc., which corresponds to a yield of about 50% of the theoretical. That it contained phenol was shown by a test with ferric chloride and by its distilling at 194.5–196°, but little above the boiling point of phenol and much below that of diphenyl ether (245°). It is believed, however, that only a small proportion of the product was phenol, because the ferric chloride test was faint, and the odor of the ether was predominant. The low boiling point was probably due to the formation of a constant boiling mixture. So much of the material was lost in unsuccessful attempts at finding a satisfactory method for purifying it that no valid estimate could be made of the relative amounts of substances present. Later in the course of the work, a good method for purifying the crude distillates was found and this method was used in the course of a detailed study of the best conditions for the preparation of diphenyl ether by this method. The results of this study will be stated at this point, though the experiments were made last in the course of the work.

The variations in conditions used were, distillation of a mixture of previously dried reagents, the addition of varying quantities of water to the mixture of dried reagents before distilling, the addition of iron filings to the mixture before distilling, and distilling at atmospheric and at reduced pressures. Several combinations of these different conditions were used, with the final decision in favor of preparing the phenolate just before using it and adding the sulfonate in the presence of enough water to keep the whole mass in solution. The use of iron filings apparently made no difference in the yield, indicating that the mixture was uniformly heated through and that probably the iron caused no reduction of the materials.

That the yield was increased by using considerable quantities of water in the mixture, indicates that in this way a better admixture of materials was obtained, either by reason of the evaporation of the solution of the mixed materials or by reason of one or both of the materials retaining water of hydration and remaining fused at the temperature at which the reaction begins. The pressure at which the distillations were made, made no difference in the yield.

The best yields obtained were close to 50% of the theoretical as crude product, and, of this, never less than 75% was obtained as pure ether.

The reason for using mixtures of sodium and potassium compounds instead of using both compounds as sodium or both as potassium salts, was that a mixture of lower melting point, and, therefore, of greater reactivity at low temperatures was expected to result in this way. A trial with sodium phenolate substituted for potassium phenolate seemed to confirm this idea both in point of temperature necessary to bring about the reaction and in point of yield. In all other experiments, the mixed salts were used.

Tolyl-p-phenyl Ether, $CH_3C_6H_4OC_6H_5$.—Fifty-two grams of potassium *p*-toluenesulfonate and 29 g. of sodium phenolate[1] were intimately mixed with one-third their bulk of iron filings and slowly distilled under reduced pressure. The crude product was a reddish brown oil with a slight green fluorescence. Yield, 49.7%. This was lost in the course of attempts to find a convenient method of purification and another distillation was made from 42 g. of the sulfonate and 23 g. of the phenolate. This was purified by steam distillation of the mixture with an excess of caustic potash solution and extraction of the distillate with ether. After drying the ether solution, it was distilled, yielding a colorless oil of a pleasant odor similar to that of diphenyl ether, boiling at 265° at 737.6 mm. Of the 51 7% of crude product obtained in the second distillation, only one-fifth was obtained as the pure ether. There is no doubt that more of it was present, but it distils so slowly with steam that enormous quantities of distillate had to be caught to get the quantity stated. If the method of purification worked out in the course of the next experiment had been known, no doubt much more could have been obtained as pure product.

(1,2)-Xylyl-p-phenyl Ether, $(CH_3)_2C_6H_3OC_6H_5$.—One hundred and four grams of sodium xylenesulfonate (1,2,4) and 66 g. of potassium phenolate were distilled under reduced pressure. The crude product, a reddish brown, fluorescent oil, represented a yield of 20%. In subsequent distillations, the yield was 50%.

Up to this point in the work, the only method for purifying the products

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[1] For this and most of the subsequent experiments, the phenolate used was prepared in bulk, dried, and kept in a tightly stoppered bottle The sulfonates were also thoroughly dried. Both were finely pulverized before being used

that could be depended on, was to distil with steam from a mixture with a solution with caustic potash in excess. The pure substances distilled very slowly with steam, as has been mentioned, and the distillate was in the form of emulsions that would not settle. This necessitated extraction with large quantities of ether. Several attempts to find simpler methods for purification had resulted in failure and loss of material, when a very satisfactory method was found while working with this ether. The crude product was warmed with solid potassium hydroxide (83% KOH) and the mixture was distilled under reduced pressure in a Bendix distilling flask. The small amount of water present distilled over at very low temperature and was easily removed completely from the receiver. The ether then distilled at constant temperature.

The purified product was a nearly colorless oil, boiling at 104–105° (cor.) at 49.4 mm. It soon solidified into short, colorless needles, melting at 35–37°. Yield, over 75% of the crude product. The ether had a pleasant odor, resembling that of diphenyl ether mixed with a little xylene. No reference could be found in the literature to any previous preparation of this ether, so it was analyzed with the following results:

Calc. for $C_{14}H_{14}O$ H = 7 02, C = 84 89   Found 7 50, 7 35, 7 1· and 84.89, 84 31, 85.11

p-Amino-diphenyl Ether, $H_2NC_6H_4OC_6H_5$.—Ninety-seven and one-half grams of sodium sulfanilate and 66 g. of potassium phenolate, mixed with one-third their total bulk of iron filings, were distilled under reduced pressure. The crude product, a reddish brown oil, was distilled from mixture with solid caustic under reduced pressure in a Bendix flask. The pure product was a pale yellow oil which soon changed into beautiful white, shining flakes. This product, amounting to 33% (pure) of the theoretical, melts at 33 34° and boils at 84° under a pressure of 15.5 mm.

o-Aminotolyl-p-phenyl Ether, $CH·(NH_2)C_6H_3OC_6H_5$.—Fifty-two grams of sodium toluidinesulfonate (1,2,5) and 33 g. of potassium phenolate, with one-third their total bulk of iron filings, were distilled under reduced pressure. The crude product amounted to a yield of 57% of the theoretical. It was purified as were xylylphenyl ether and amino-diphenyl ether, yielding a pale yellow oil amounting to about half the crude material. Boiling point, 102–104° at 67.4 mm. Unlike the amino-diphenyl ether, it did not solidify on standing, but darkens in the light. It has an odor similar to that of aniline, but not quite so disagreeable, when freshly distilled, and takes on a phenol-like odor on standing. No reference to the preparation of this compound could be found in the literature, so its nitrogen content was determined by the Kjeldahl method.

Calc. for $C_{13}H_{13}ON$: N = 7.02. Found: 7.18 and 7.22.

This was considered sufficient analytical data to establish its probable

formula, since there was no apparent difference in the course of its preparation and that of its lower homolog just described, and the melting point of the simpler compound was as given in the literature.

Thymyl-phenyl Ether, $CH_3(C_3H_7)C_6H_3OC_6H_5$.—An amount of potassium hydroxide equivalent to 14 g. of the anhydrous compound, 37.5 g. of thymol, and 45 g. of sodium benzenesulfonate were dissolved together in a small quantity of water and distilled. The water distilled off first, and was followed by a yellowish brown oil. This latter was redistilled as usual and the resultant colorless oil had a strong odor like that of thymol with a faint modification toward that of diphenyl ether. Its boiling point was found somewhat lower·than that given for this compound by Ullman and Sponagel,[1] 289° as compared to 297°, but it all distilled within a degree.

It was suggested that the identification of this compound as thymyl-phenyl ether was not complete in view of its low boiling point. The quantity of it formed was too small to permit of further experiments with it, so the experiment was repeated, with the difference that it was purified by distillation with steam, extraction of the steam distillate with ether, and distillation of the residue after removal of the ether. The residue from the ether solution amounted to nearly 10 cc., of which 6 cc. distilled below 290° (only two or three drops came over below 287°) and the remainder came over between 294° and 295°, leaving a slight brown stain in the distilling bulb. The color of the distillate, however, was much darker than that of the residue from the ether and its odor was much sharper.

If thymyl-phenyl ether is formed by the reaction, it is decomposed by the high temperature, and the quantity obtained is too small to admit of clear identification.

Anisole, $CH_3OC_6H_5$.—An amount of potassium hydroxide equivalent to 14.3 of the anhydrous compound and 23.5 g. of phenol were dissolved together in the retort and 29 g. of sodium methylsulfonate were added. The sulfonate used was prepared by the method given in German patent No. 55,007.[2] The behavior during distillation differed, in this case, from the others only in that a larger part of the oil came over with the aqueous portion of the distillate. The crude product had a pronounced odor of anisole and measured up to a yield of 100% of the theoretical. It was purified by distillation with steam from caustic mixture—the oil separating readily from the water. After drying with calcium chloride, the ether was distilled and found to come over completely between the temperatures 149-152°. The yield of pure anisole (volume of the oil separated from the steam distillate) was 55%.

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[1] *Loc. cit.*

[2] Lassar-Cohn, *Arbeitsmethoden für Organisch-Chemische Laboratorien*, 4te. Aufl. spes. Tl., p. 1324

Attempts were made to prepare the mono- and diphenyl ethers of resorcin and the phenyl ethers of α- and β-naphthols. The work is as yet incomplete.

Summary.

1. Dry distillation of alkali salts of sulfonic acids with alkali phenolates is a convenient method for the preparation of aryl ethers of phenols. Though the yields are considerably less than those obtained by the method of Ullman and Sponagel, the compounds used can, in some cases, be more directly prepared.

. 2. The reaction probably proceeds according to the equation

$$RSO_3M + R'OM = R'OR + M_2SO_3,$$
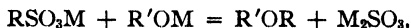
in which equation, the symbol R may represent the phenyl radical and its homologs, provided no long side-chain is present, or a methyl group. The symbol R' represents a phenyl radical or an aminophenyl radical. The presence of a long side-chain in this radical interferes with the reaction's proceeding normally or causes decomposition of the product

LEXINGTON, KY

RESEARCHES ON PYRIMIDINES. LXXII. THE SYNTHESIS OF 4-HEXYLURACIL AND ITS RELATIONSHIP TO URACIL-GLUCOSIDE.

BY TREAT B JOHNSON
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1. Pyrimidine-Nucleosides: The Structure of Uridine.

The elucidation of the structure of nucleic acids obviously involves the determination of the constitution of *nucleosides*. The latter are characteristic purine-carbohydrate and pyrimidine-carbohydrate combinations, which result by partial hydrolysis of these naturally occurring acids. We have practically no knowledge regarding the nature of the carbohydrate linkings in these compounds, and, consequently, we are unable to express structually their exact constitution. One important fact, however, seems to have been very definitely established by the results already obtained, namely, that the two nitrogen cycles—the purines and pyrimidines—are not joined to the carbohydrates in a similar manner. The experimental data, thus far obtained, suggest that the sugar, in the case of the purine-nucleosides, is very probably linked to the purine at a nitrogen atom occupying either the 7- or the 9-position of the purine ring. Such hexose combinations have recently been synthesized by Emil Fischer[1] and it is interesting to note that his synthetical glucosides agree

[1] Fischer and Helferich, *Ber.*, **47**, 210 (1914).

very closely, in chemical behavior, with that of the naturally occurring purine-nucleosides. This investigator has not established, however, whether the carbohydrate is joined, in his synthetical products, to the purine ring at positions 7 or 9.

Whether the pyrimidines—uracil, thymine and cytosine—are linked to carbohydrates, in pyrimidine-nucleosides, through one of the nitrogen atoms in positions 1 and 3 of the ring is indeed questionable. Surely the remarkable stability of the natural nucleosides towards hydrolytic agents does not support such an assumption. It has been our experience in this laboratory that such glucosidic combinations, as are represented by the general formulas (I and II), are very unstable and easily undergo hydrolysis

```
      HO
      |
R—CH.N—CO                         NH—CO
      |    |                       |    |
      CO   CH                HO    CO   CH
      |    ||                 |    |    ||
      NH—CH                  R—CH.N——CH
      (I)                            (II)
```
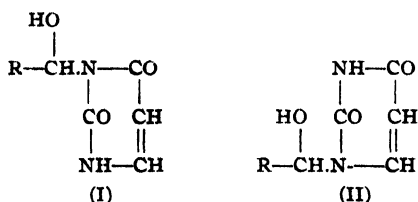
in the presence of acids, and even boiling water, giving the original pyrimidine. Several combinations of these types have been synthesized by us, but, in no case which has thus far been carefully examined have we obtained a stable compound. These observations have recently been confirmed by the results obtained by Fischer[1] in his investigations on pyrimidine-glucosides. It seems safe to assume, however, if a nitrogen-carbon linkage is found to be present, that the combination which involves the nitrogen atom in position 3, as represented by Formula II, will be found to be the most resistent to the action of hydrolytic agents. Whether the higher, synthetical, glucosidic combinations of this type will approach in stability that of the pyrimidine-nucleosides remains to be established.

The early observation that pyrimidine-combinations corresponding to Formulas I and II easily break down on hydrolysis with acid, and the interesting conclusion of Levene and La Forge[2] that the constitutions of cytidine and uridine are possibly to be expressed by Formulas III and IV, respectively, led us to turn our attention to the study of simple pyrimi-

```
N = C.NH₂                          NH—CO
|    |                             |    |
CO   CH                            CO   CH
|    ||  ┌———O-———┐                |    ||  ┌———O———┐
NH—C.CH.CHOH.CHOH.CH.CH₂OH         NH—C.CH.CHOH.CHOH.CH.CH₂OH
       (III)                              (IV)
```
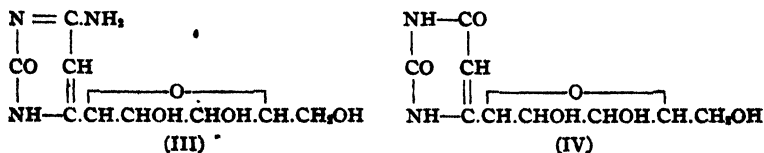
[1] Ber., 47, 1377 (1914).
[2] Ibid., 45, 608 (1912).

$$\text{OH}$$

dine-nucleosides containing the glucosidic union R.CH— in the 4-position of the pyrimidine ring. No representative of this class of pyrimidines had been described in the literature previous to our investigations. This work has proved very fruitful from a synthetical standpoint. A method of synthesizing pyrimidines of this type has now been developed which has enabled us to obtain the simplest nucleosides of thymine (V) and uracil (VI). A description of these interesting compounds has been recorded in papers from this laboratory [1]. The synthesis and properties of a higher homolog of uracil-nucleoside (VI) will be discussed in a future publication.

```
NH--CO                    NH--CO
 |    |                    |    |
CO    C CH₃               CO    CH
 |    ||                   |    ||
NH—C CH.OH                NH—C CH₃OH
   (V)                       (VI)
```
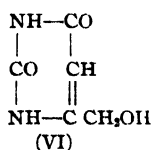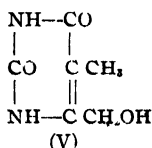
Our method of establishing the constitution of these two synthetical nucleosides (V and VI) was to subject them to the action of strong hydriodic acid, when they underwent reduction smoothly giving 4,5-dimethyluracil (VII) and 4-methyluracil[2] (VIII), respectively. The success of this

```
NH—CO                     NH--CO
 |    |                    |    |
CO    C CH₃               CO    CH
 |    ||                   |    ||
NH—C CH₄                  NH—C CH₃
   (VII)                     (VIII)
```
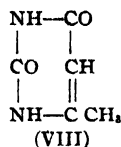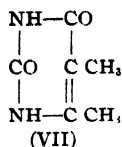
method of identifying hydroxylated derivatives of this type is dependent essentially upon two facts, firstly, that the double bond in uracil compounds is not destroyed by digestion with hydriodic acid, and secondly, that the 4-alkyl substituted uracils, so far as examined, possess such characteristic properties that they can be easily identified, even when working with small amounts of material. Whether the higher homologs of these two nucleosides will be found to interact normally with hydriodic acid remains to be established, but it is certain from what is already known that it should be possible theoretically to accomplish such changes. A knowledge of the properties of the higher homologs of 4-methyluracil and the corresponding thymine compounds is, therefore, very essential.

I find no record, in the papers of other investigators, that any attempts have been made to reduce uridine (IV) or cytidine (III) with hydriodic

[1] Johnson and Chernoff, *J Biol Chem*, **14**, 307 (1913); THIS JOURNAL, **35**, 585 (1913); **36**, 1742 (1914)

[2] Johnson and Chernoff, *loc. cit.*

acid.   Reduction of uridine in the presence of palladium[1] leads to the forma-
tion of the corresponding hexahydro derivative with destruction of the
double bond between the carbons in positions 4 and 5 of the pyrimidine
ring.   According to Formula (IX) uridine is a monosubstitution product
of the alcohol xylite, $C_5H_{12}O_5$ (X), while the relationship between Levene's
formula for uridine, and that of isosaccharic acid is apparent by inspection
of their respective formulas (IV and XI).   Theoretically then, there is
no reason to assume that these related compounds should undergo re-
duction otherwise than in an analogous manner, giving their corresponding
alkyl derivatives.   Bertrand[2] has shown that xylite is transformed into
iodopentane, $CH_3.CHI.CH_2.CH_2.CH_3$, by reduction with hydriodic acid,
while isosaccharic acid (XI), which is prepared from chitosamine, by
oxidation with nitric acid, and also from chitine,[3] is reduced to adipic acid
(XII), when heated with hydriodic acid at 140–150°.   The reduction,
therefore, of a pyrimidine having either the constitution IV or IX to
4-pentyluracil (XIII) would be a perfectly normal reaction.   The forma-

NH—CO
CO   CH OH OH OH OH OH
NH—C . CH.CH.CH.CH.CH₂

(IX)

OH   OH OH OH OH
CH₂.CH.CH CH.CH₂
(X)

CH₃.CH₂.CH₂.CH₂.CH₃

NH—CO
CO   CH
NH—C—CH₂.CH₂.CH₂.CH₂.CH₃
(XIII)

NH—CO
CO   C
NH—C—CH   CH.CH₂OH
HOCH—CHOH
(IV)

┌–O–┐
HOOC.CH   CHCOOH
HOCH—CHOH
(XI)

HOOC.CH₂.CH₂.CH₂.CH₂.COOH
(XII)
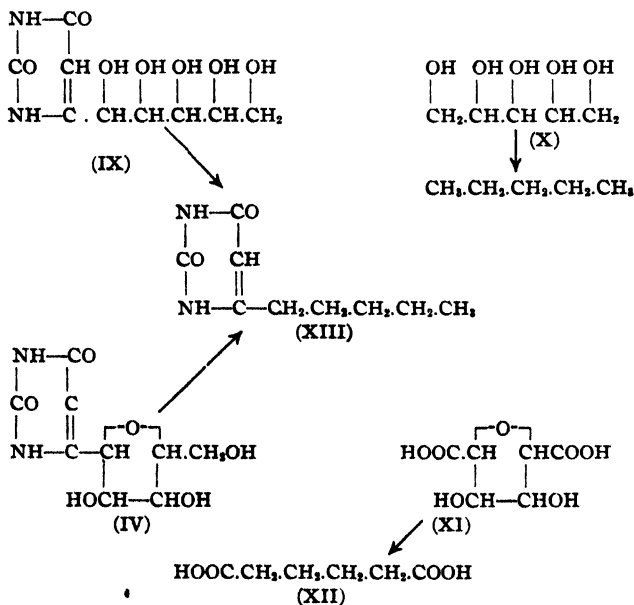
tion of this alkylated uracil from uridine would establish, beyond doubt,
the correctness of Levene's Formula (IV).   An investigation dealing with

[1] Levene and La Forge, loc. cit.
[2] Bull. soc. chim., [3] 5, 556, 740 (1891)
[3] Tiemann and Haarmann, Ber., 17, 246 (1884); 19, 1257 (1886); Tiemann, Ber.,
27, 118 (1894)

the synthesis of this unknown uracil derivative (XIII), is now in progress in this laboratory. In the following chapter of this paper is given a description of the synthesis and properties of the next higher homolog of 4-pentyluracil, namely, *4-hexyluracil* (XV), which would be the reduction product of a corresponding hexose uracil-nucleoside represented by Formula XIV

$$
\begin{array}{l}
\text{NH—CO} \\
\mid \quad \mid \\
\text{CO} \quad \text{CH} \\
\mid \quad \parallel \quad \lceil \text{————O————} \rceil \\
\text{NH—C—CH CHOH CHOH CH CHOH CH}_2\text{OH} \\
\qquad\qquad \downarrow \text{(XIV)}
\end{array}
$$

$$
\begin{array}{l}
\text{NH—CO} \\
\mid \quad \mid \\
\text{CO} \quad \text{CH} \\
\mid \quad \parallel \\
\text{NH—C CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_3 \\
\qquad\qquad \text{(XV)}
\end{array}
$$
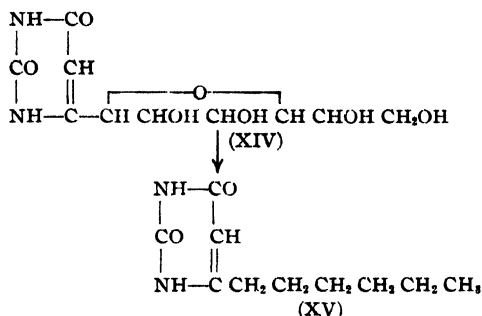
In Table I, below, is listed a series of some higher polyatomic alcohols and their oxidation products, which have been shown to undergo reduction normally with hydriodic acid

TABLE I

Hydroxyl Derivative	*Reduction Product*
Xylite,[1] $HOCH_2(CHOH)_3 CH_2OH$	$\longrightarrow$ $CH_3 CHI_2 CH_2 CH_2 CH_3$.
Styracite,[2] $C_6H_{12}O_6$	$\longrightarrow$ hexyliodide
Mannite,[3] $HO CH_2(CHOH)_4 CH_2OH$	$\longrightarrow$ hexyliodide
Sorbit,[4] $C_6H_{14}O_6$	$\longrightarrow$ hexyliodide
Mannoheptite,[5] $C_7H_{16}O_7$	$\longrightarrow$ heptyliodide
Rhamnonic acid,[6] $CH_3(CHOH)_4COOH$	$\longrightarrow$ caproic acid
l-Mannonic acid,[7] $HOCH_2(CHOH)_4COOH$	$\longrightarrow$ caproic acid
d-Galactonic acid[8]	$\longrightarrow$ Lactone of caproic acid
α-Rhamnohexonic acid,[9] $CH_3(CHOH)_5COOH$	$\longrightarrow$ heptylic acid
α-Glucoheptonic acid,[10] $HOCH_2(CHOH)_5COOH$	$\longrightarrow$ heptylic acid
d-Mannoheptonic acid[11]	$\longrightarrow$ heptylic acid

[1] Bertrand, *loc cit*

[2] Ashina, *Chem Zentr*, 1907, II 1431, 1909, II, 548, *Ber*, **45**, 2363 (1912)

[3] Erlenmeyer and Wanklyn, *Ann*, 111, 247 (1859) Hecht, *Ber*, 11, 1420, 1152 (1878), Schorlemmer, *Ann*, 199, 141 (1879)

[4] Vincent and Delachanal, *Compt rend* 108, 354 (1889), 111, 51 (1980), Hitzemann and Tollens, *Ber*, 22, 1048 (1889)

[5] Maquenne, *Bull soc chim*, [2] 50, 132, 548 (1888), *Ann chim phys*, [6] 19, 5 (1890)

[6] Will and Peters, *Ber*, 21, 1813 (1888), 22, 1704 (1889)

[7] Kiliani, *Ber*, 20, 339 (1887), 19, 3034 (1886)

[8] Kiliani, *loc cit*

[9] Fischer and Tafel, *Ber*, 21, 2175 (1888)

[10] Kiliani, *Ber*, 19, 1128 (1886)

[11] Fischer and Hartmann, *Ber*, 22, 372 (1889)

TABLE I (continued).

Hydroxyl Derivative.	Reduction Product.

$$\text{Laevuloheptonic acid,}[1]\ \text{HOCH}_2(\text{CHOH})_3.\overset{\displaystyle\overset{\text{OH}}{|}}{\underset{\displaystyle\underset{\text{COOH}}{|}}{\text{C}}}\text{—CH}_3\text{OH} \longrightarrow \alpha\text{-methylhexylic acid}$$

Saccharic acid,[2] HOOC.(CHOH)$_4$COOH $\longrightarrow$ adipic acid

Mucic acid,[3] HOOC(CHOH)$_4$COOH $\longrightarrow$ adipic acid

Isosaccharic acid[4] $\longrightarrow$ adipic acid

2. The Synthesis of Normal 4-Hexyluracil.

It is 31 years since the publication of Behrend's classic paper entitled: "Über die Einwirkung von Harnstoff auf Acetessigäther (Vorläufige Mittheilung),"[5] and 27 years since List[6] showed that 2-thiouracil is formed by condensation of ethyl acetoacetate with thiourea. Since the appearance of these papers a great number of derivatives of ethyl acetoacetate have been shown to undergo condensation with urea compounds forming pyrimidines, but, notwithstanding this activity, no one has shown, thus far, that the higher homologs of ethyl acetoacetate (Table II) functionate

TABLE II.

Ethyl propionylacetate, $CH_3CH_2COCH_2COOC_2H_5$

Ethyl butyrylacetate, $CH_3CH_2CH_2COCH_2COOC_2H_5$

Ethyl valerianylacetate, $CH_3 CH_2CH_2CH_2COCH_2COOC_2H_5$

Etc.

normally and condense with urea and thiourea, giving the corresponding 4-alkyl derivatives of uracil and thiouracil, respectively. We have no knowledge of the higher homologs of 4-methyluracil or 2-thio-4-methyluracil. In fact, no representative of the two homologous series of pyrimidines, represented in Table III below, have been described in the literature except the 4-methyl derivatives. The other members of these two series which are now of immediate biochemical interest, are the lower representatives, and especially the 4-pentyl and 4-hexyl derivatives of uracil, which may be considered as the reduction products of the corresponding pentose and hexose glucosides of this pyrimidine.

The starting point in our synthesis of 4-hexyluracil (XV) was the β-ketone ester *ethyl heptylylacetate* (XVI), which is now easily obtainable, if ethyl heptylate is available, by condensation of this ester with ethyl acetate.[7] For all the ester, however, which was used in this research, I

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[1] Kiliani, *Ber.*, 19, 224 (1886)

[2] de la Motte, *Ber.*, 12, 1571 (1879).

[3] Crum-Brown, *Ann.*, 125, 19 (1863); Heinzelmann, *Ibid.*, 193, 184 (1878).

[4] Tiemann and Haarmann, *loc. cit.*

[5] *Ber.*, 16, 3027 (1883)

[6] *Ann.*, 236, 1 (1887)

[7] Wahl and Doll, *Bull. soc chim.*, 13, 265 (1913).

TABLE III

Pyrimidines   *Thiopyrimidines*
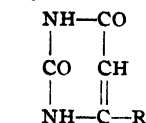
$$\begin{array}{cc} NH\!-\!CO \\ |\quad\ | \\ CO\quad CH \\ |\quad\ || \\ NH\!-\!C\!-\!R \end{array} \qquad (R = CH_3, C_2H_5, etc) \qquad \begin{array}{cc} NH\!-\!CO \\ |\quad\ | \\ CS\quad CH \\ |\quad\ || \\ NH\!-\!C\ R \end{array}$$
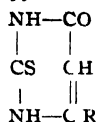
1 $C_5H_6O_2N_2$ 1 $C_5H_6ON_2S$
(Methyluracil)   (Methylthiouracil)

2 $C_6H_8O_2N_2$ 2 $C_6H_8ON_2S$
(Ethyluracil)   (Ethylthiouracil)

3 $C_7H_{10}O_2N_2$ 3 $C_7H_{10}ON_2S$
(Propyluracil)   (Propylthiouracil)

4 $C_8H_{12}O_2N_2$ 4 $C_8H_{12}ON_2S$
(Amyluracil)   (Amylthiouracil)

5 $C_9H_{14}O_2N_2$ 5 $C_9H_{14}ON_2S$
(Pentyluracil)   (Pentylthiouracil)

6 $C_{10}H_{16}O_2N_2$ 6 $C_{10}H_{16}ON_2S$
(Hexyluracil)   (Hexylthiouracil)

↓

Etc   I tc

am indebted to Professor Andre Wahl, of Saint Denis (Seine), France I take this opportunity to express here my appreciation of his cooperative spirit and kindness in sending me this reagent   When this ketone ester is warmed with thiourea in an alcoholic solution of sodium ethylate there is an immediate reaction with formation of the sodium salt of 2 thio-4-hexyluracil (XVII)   The reaction is complete after boiling for a few hours, and, after evaporation of the alcohol, the free pyrimidine is then easily obtained by decomposing its sodium salt with hydrochloric acid   A description of this compound is given in the experimental part of this paper   The reaction may be expressed by the following equation

$$\begin{array}{cc} NH_2 & COOC_2H_5 \\ | & | \\ CS\ + & CH_2 \\ | & | \\ NH_2 & OC\ CH_2CH_2CH_2CH_2CH_2CH_3 \\ & (XVI) \end{array} \quad = H_2O + C_2H_5\,OH$$

$$+\ \begin{array}{cc} NH\!-\!CO \\ |\quad\ | \\ CS\quad CH \\ |\quad\ || \\ NH\!-\!C\ CH_2CH_2CH_2CH_2CH_2CH_3 \\ (XVII) \end{array}$$
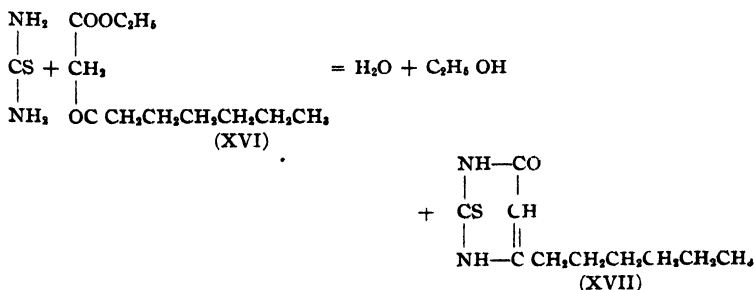
4-Hexyluracil (XV) is easily obtained by direct desulfurization of this 2-thiopyrimidine (XVII)   This is easily accomplished by digesting the

sulfur compound with an excess of chloroacetic acid in aqueous solution. Complete desulfurization is effected within a few hours and the yield of 4-hexyluracil is practically quantitative. This new pyrimidine possesses a sharp, definite melting point (170°), and is especially characterized by its crystalline habit and insolubility in cold water. A complete description of this interesting substance is given in the experimental part of this paper.

```
NH—CO                                    NH—CO
|    |              CICH₂COOH            |    |
CS   CH          ───────────►           CO   CH
|    ||                                   |    ||
NH—C.CH₂CH₂CH₂CH₂CH₂CH₂CH₃              NH—C.CH₂CH₂CH₂CH₂CH₂CH₃
      ·                                            (XV)
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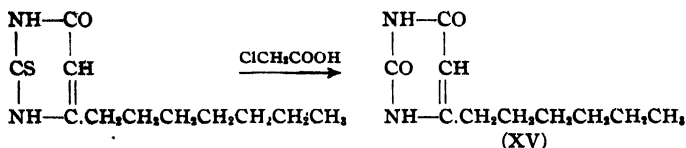
The study of pyrimidine-nucleosides and related compounds will be continued.

3. Experimental Part.
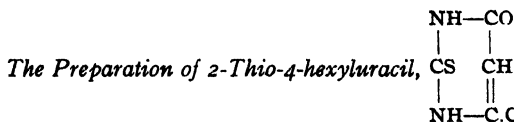
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                                        NH—CO
                                         |    |
The Preparation of 2-Thio-4-hexyluracil, CS   CH
                                         |    ||
                                        NH—C.CH₂ CH₂ CH₂ CH₂ CH₂ CH₃
```

—This pyrimidine is easily obtained by condensation of thiourea with ethyl heptylacetate.[1] Two molecular proportions of sodium (1.0 g.) were dissolved in 25 cc. of absolute ethyl alcohol, 5 g. of the β-ketone ester dissolved in the solution, and the mixture then heated with 4.0 g. of thiourea (an excess), at the temperature of the steam bath, for 3 hours. A turbid solution was obtained. The alcohol was then removed by heating in an open dish at 100° and the crude reaction product dissolved in about 30 cc. of cold water and the solution filtered. On acidifying this alkaline solution with a slight excess of dilute hydrochloric acid the above 2-thiopyrimidine separated as an oil which very soon solidified. It was nearly colorless and the yield was excellent. This pyrimidine was purified by recrystallization from boiling water. It is difficultly soluble in this solvent and deposits, on cooling, in beautiful, colorless needles which melt at 145° to a clear oil without effervescence. The pyrimidine gave a strong test for sulfur. Nitrogen determination:

Calc. for C₁₀H₁₆ON₂S: N, 13.20; found: N, 13.08.

The above experiment was repeated using the following proportions: 8 g. of the β-ketone ester, 6.4 g. of thiourea, 1.6 g. of sodium and 50 cc. of absolute alcohol. After digesting for 6 hours, the reaction was apparently complete. The alcohol was then removed in the usual manner and the pyrimidine precipitated from its aqueous salt solution by addition of

[1] Wahl and Doll, *loc. cit.*

hydrochloric acid   The crude pyrimidine melted at 140–141° and the yield was about 4 5 g

Desulfurization of 2 Thio 4 hexyluracil with Formation of 4 hexyluracil,
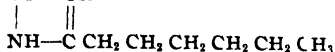
NH—CO
|
CO   CH   —The best conditions for the successful
| ||
NH—C CH₂ CH₂ CH₂ CH₂ CH₂ CH₃

conversion of the 2 thiopyrimidine into this pyrimidine are as follows
Equal parts by weight of the thiopyrimidine and monochloroacetic acid are dissolved in about 12–13 times their combined weight of water (4 g of pyrimidine to 100 cc of water) While the chloro acetic acid dissolves immediately at ordinary temperature it is necessary to boil for several minutes before solution of the pyrimidine is effected   After complete solution of the pyrimidine the mixture is then boiled for several hours   After solution of the pyrimidine it is best to add about 10 cc of dilute hydrochloric acid to aid the reaction   After digesting for about 7–8 hours (working with 4 g of pyrimidine) the re action is complete, and, on cooling the solution hexyluracil separates as an oil which soon solidifies   This pyrimidine is extremely insoluble in boiling water and separates on cooling in beautiful glistening plates which melt at 170° to a clear oil without effervescence   The yield is practically quantitative   The pyrimidine did not lose weight when heated at 110–120°, and did not respond to a test for sulfur   Nitrogen determination

Calc for $C_{10}H_{16}O_2N$ N 14 29 found N 14 15

This pyrimidine is extremely soluble in alcohol and separates in plates when an alcoholic solution is diluted with water   It dissolves also in sodium hydroxide solution

NEW HAVEN CONN

THE ACTION OF NITRIC ACID ON IODOANIL.

BY LATHAM CLARKE AND E K BOLTON [1]
Received July 10 1914

Owing to the absence from the country of both the authors it has been necessary for me to prepare this work for publication —C I JACKSON

The object of the work described in this paper was to compare the behavior of iodoanil and chloroanil with nitric acid   Stenhouse[2] obtained from the latter chloropicrine and oxalic acid   As he found that chloroanilic acid behaved in the same way, and that bromoanilic acid gave bromo-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton
[2] *J Chem Soc* 8, 6 (1870)

picrine and oxalic acid, it is probable that bromoanil would undergo a similar reaction; but our experiments show that the action with iodoanil is entirely different, since nitric acid converts it into iodine pentoxide and diiodomaleic acid; and this difference is due to the nature of the substances, not to a less energetic action in our experiments than in those of Stenhouse, since we used fuming nitric acid instead of the strong acid used by him, and heated the mixture on the steam bath from 4 to 5 hrs., followed, after the removal of the iodine pentoxide, by evaporation of the acid from 300 to 50 cc. Therefore, if the diiodomaleic acid were only an intermediate stage in the formation of iodopicrine and oxalic acid, we must have obtained some of these products, but the most careful search revealed no trace of them.

. The identification of the diiodomaleic acid was not an easy matter. We could find no method of purifying it in spite of many and varied attempts, and the analyses gave bad results, which were explained in part by the formation of the anhydride, as we found that this substance was formed by long standing *in vacuo*; but only in part, since the anhydride gave equally bad analytical results, and also melted 4° lower than the specimen prepared by Diels and Reinbeck.[1] It seems, therefore, that both our acid and anhydride contained some clinging impurity, which we could not remove by crystallization. The composition of our two substances was, however, established by determinations of the molecular weight of the anhydride, and analyses of the sodium salt and aniline salt of the acid, of several of its other derivatives, and by titrations, which showed that it was dibasic. Three different compounds agree with these results, diiodosuccinic acid, diiodomaleic acid, and diiodofumaric acid. The last of these can be rejected at once, since our acid forms an anhydride easily. For instance, on heating the acid with toluene, in which it is insoluble, it gradually went into solution, while at the same time a drop of water appeared in the toluene, and upon evaporating the solvent, the anhydride already mentioned was obtained. The decision between the maleic and succinic acid was more difficult. Our compound did not act with bromine, but this has no weight, as it has been shown[2] that the presence of a halogen frequently interferes with the addition of bromine to an unsaturated acid. The potassium permanganate test for a double bond could not be applied, since it decomposed our acid with liberation of iodine—a behavior frequently observed even with saturated iodine compounds; reducing agents also gave no definite results with it, so that it was impossible to settle the question by experiment. In spite of this, however, it seems to us that the following considerations exclude diiodosuccinic acid: To form this com-

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[1] *Ber.*, **43**, 1271 (1910).

[2] Bauer, *Ber.*, **37**, 3317 (1904); Pum, *Monats.*, **9**, 449 (1888).

pound from iodoanil it would be necessary to add two atoms of hydrogen to that substance, which would obviously be impossible in the presence of hot, fuming nitric acid   The diiodosuccinic acid has not as yet been prepared, and it may be doubted whether it is stable enough to exist, as Finkelstein[1] obtained by the action of sodium iodide on dibromosuccinic acid in acetone solution, sodium bromide iodine, and fumaric acid, and Brunner and Chuard found the same products on treating monobromosuccinic acid with potassium iodide in alcohol   Our somewhat impure diiodomaleic anhydride melts 4° below the pure compound made by Diels and Reinbeck,[3] but at least 20° higher than the known dihalogen succinic anhydrides

On the other hand, our anhydride differs from that described by Diels and Reinbeck in two particulars besides the melting point   They state it is yellow and insoluble in benzene, whereas we found it white, turning yellow on exposure to air, and soluble in benzene in sharp contrast to the insolubility of the diiodomaleic acid   Skraup[4] has found that maleic acid is converted into fumaric acid by heating it with strong nitric acid, but, although our acid was submitted to the long continued action of hot, fuming nitric acid, we obtained only maleic acid (shown by its easy conversion into an anhydride), it seems, therefore, that the presence of the two atoms of iodine in our acid must prevent this transformation

So far as we can find, this is the first time that maleic acid has been formed from a substituted quinone by nitric acid, but the reaction has been brought about by other reagents[5]

If the acid aniline diiodomaleate is suspended in glacial acetic acid, and heated, it is converted into the diiodomaleylphenylimide (or anil), which must have the ring formula given below   It melts at $171-172°$ (uncor)

$$
\begin{array}{l}
IC \quad CO \\
\| \qquad > NC_6H_5 \\
IC - CO
\end{array}
$$
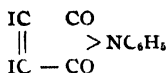
By the further action of aniline in alcoholic solution, this substance is converted into the phenylaminomaleylphenylimide (anilinomaleylanil), melting at $232-233°$ (uncor) which has been made frequently before, and found to melt at $230°,$[6] $231°$[7] $232-233°,$[8] or $235°$[9] Dichloro or dibromomaleic acid, when treated with aniline retains one atom of halo

[1] *Ber* **43**, 1528 (1910)

[2] *Ibid* **30**, 200 (1897)

[3] *Ibid* **43**, 1271 (1910)

[4] *Monats* **11**, 323 (1890) **12**, 124 (1891)

[5] Zincke Fuchs *Ann* **267**, 1 (1892) Kempf *Ber* **39**, 3715 (1906)

[6] Michael *Ber* **19**, 1377 (1886)

[7] Reissert Tiemann *Ber* **19**, 622 (1886) Reissert *Ibid* 1644 (1886)

[8] Wohl Freund *Ber* **40**, 2300 (1907)

[9] Bischoff Walden *Ann* **279**, 140 (1894)

gen,[1] which is in harmony with the observation frequently made in this laboratory that iodine is replaced by hydrogen more easily than bromine, bromine than chlorine

p-Toluidine gave with diiodomaleic acid *p*-tolylaminomaleyl-*p*-tolyl imide, which we found to melt at 229° (uncor) Junghahn and Reissert[2] found 228° Phenylhydrazine gave, with diiodomaleic acid, as the prin cipal product diiodomaleylphenylhydrazide melting at 170° (uncor) and in smaller quantity a substance melting at 266 267° (uncor), which we suppose to be phenylhydrazomaleylphenylhydrazide, but did not obtain enough of it to settle its composition

When the diiodomaleic acid was heated with water to 100° in a sealed tube, we obtained carbon dioxide, formaldehyde, hydriodic acid, and a little free iodine, and in addition to these soluble compounds a brown oil, solidifying on standing, from which two white solids were obtained One gave a percentage of iodine agreeing with that for diiodoacetic acid, but as it was white, and melted at 95–96° (uncor), we cannot consider its nature settled, since diiodoacetic acid is pale yellow, and melts at 110°[3] Unfortunately, this work was begun so late in the year that we had not time enough to find the explanation of this discrepancy For the same reason we can give only a preliminary account of the second substance, melting at 182–184° (uncor) A single determination of iodine indi cates that it is the as yet undiscovered pentaiodoethane

Experimental.

*Action of Fuming Nitric Acid on Iodoanil —*Thirty-five grams of crude iodoanil were mixed with 300 cc of nitric acid of specific gravity 1 50, and heated on a sand bath to slow boiling in a flask fitted by a ground joint to an air return condenser After half an hour a white solid separa ted, which increased in amount, as the reaction continued At the end of 4 or 5 hrs , after the brown color of the iodoanil had disappeared, the orange-red acid solution was allowed to cool, and decanted from the white solid, which was washed with a little strong nitric acid, the washings being added to the main portion of the acid This white solid showed the proper ties of iodine pentoxide, as it sublimed at about 300° with partial decom position into iodine and oxygen, but gave off no water, absorbed moisture from the air changed its cream color to the pure white of iodic acid, and its strongly acid aqueous solution set free chlorine from hydrochloric acid, or iodine from potassium iodide It was prepared for analysis by washing with glacial acetic acid, drying *in vacuo* over potassium hydroxide, and finally washing with benzene and drying *in vacuo*

Calc for I_2O_5 I, 76 04, found I, 76 00, 75 90

[1] Michael *Am Chem J* **9,** 180 (1867), Anschutz, Beavis, *Ann ,* **295,** 29 (1897); Salmony Simonis *Ber* **38,** 2580 (1905)

[2] *Ber* **24,** 1766 (1891)

[3] Angeli, *Ber ,* **26,** 596 (1893)

35 g of the iodoanil gave 26 g of iodine pentoxide

For further identification the aniline iodate was made by adding a mixture of aniline and alcohol to an aqueous solution of the acid   The precipitate formed was washed with alcohol and benzene

Calc for $C_6H_5NH_2HIO_3$ I 47 18 found I 47 87

The analysis was attended with difficulty, because the salt explodes violently, when brought in contact with nitric acid so that only one of the Carius tubes used by us escaped being blown to pieces   Our observations confirm the properties of the salt as given by Beamer and F W Clarke,[1] the explosiveness with nitric acid, and the fact that the crystals turn blue on exposure to the air being the only points we have to add to their description

Diiodomaleic Acid   The orange red acid solution poured off from the iodine pentoxide was evaporated on the steam bath until reduced to about 50 cc , when it was freed from any additional iodine pentoxide by decantation, or if necessary, filtration through glass wool covered with a thin layer of asbestos, and allowed to cool   Rosets of long, white needles separated, which were filtered out on a fine Buchner filter and freed from adhering acid by a porous plate and standing in a desiccator over potassium hydroxide   A second crop of crystals was obtained by evaporating the filtrate to 25 cc , but further evaporation yielded only a small additional amount contaminated with iodine pentoxide   No test for oxalic acid was obtained from the solution   From 35 g of iodoanil 11 g of the crystals were obtained, or 52% of the theoretical yield, if one molecule of the product was obtained from each molecule of iodoanil   This product was recognized as diiodomaleic acid by analyses of some of its derivatives given later   No good analyses of the acid itself could be obtained, the percentages of iodine and of carbon coming out somewhat over 1% too high for the theory   This was in part due to formation of anhydride during the drying *in vacuo,* as a specimen which stood *in vacuo* for one week showed an increase of o 8% in its iodine, but this was not the only reason, as our analyses of the anhydride were even worse, coming out not far from 2% too high on both the iodine and carbon   We have not found any method for the purification of the diiodomaleic acid, as no good results could be obtained from crystallizations even from mixed solvents, or precipitations from its solutions, and once dissolved it could be recovered only by evaporation to dryness   Benzene with alcohol, and acetone with chloroform were tried with especial care, other combinations less thoroughly   Strong sulfuric acid precipitated the compound from its aqueous solution, but failed to purify it, strong hydrochloric acid did not even precipitate it   The acid formed by the action of water on the

[1] *Ber* , **12,** 1066 (1879)

anhydride gave no better results on analysis than the acid as formed direct from nitric acid.

Properties of Diiodomaleic Acid, $C_2I_2(COOH)_2$.—It crystallizes from fuming nitric acid in rosets of long, white needles. Our best specimens melted at 142° with evolution of bubbles, and the formation of a pale yellow liquid, but the true melting point is undoubtedly higher, as the analyses showed that our substance was not pure, containing the anhydride undoubtedly, and probably a second impurity. It is very soluble in water, methyl or ethyl alcohol, ether, acetone, glacial acetic acid, acetic ester, or nitrobenzene; insoluble in chloroform, carbon tetrachloride, carbon disulfide, benzene, toluene, or naphtha. No good solvent could be found for it. Boiling benzene, or toluene, converts it into the anhydride, which dissolves as it forms. The acid is less soluble in sulfuric acid than in water.

The aqueous solution of the diiodomaleic acid gave an acid reaction with litmus and decomposed carbonates with effervescence. A specimen crystallized from the nitric acid was dried on a porous plate and then *in vacuo* over potassium hydroxide, and washed several times with warm benzene, after which it was titrated with a 0 2 N potassium hydroxide solution, using phenolphthalein as the indicator.

Subst I, 1 1120, 0 540 g , II, 0 847, 0 764 g , KOH, 0 373, 0 180, 0 285, 0 257. Number of carboxyl groups, 2 1, 2 1, 2 1, 2 1

The acid is therefore dibasic. II was a specimen prepared from the anhydride with water.

Sodium Diiodomaleate, $C_2I_2(CO_2Na)_2$.—Three grams of diiodomaleic acid, dissolved in 50 cc. of absolute alcohol, were treated with sodium ethylate[1] as long as a precipitate was formed. The salt was washed six times with alcohol and dried *in vacuo*.

Subst 0 5856, 0 7417 g , Na₂SO₄, 0 2080, 0 2645 g , calc for $C_2I_2(CO_2Na)_2$ Na, 11.16, found Na 11 50, 11 55

It forms small, white plates soluble in water but insoluble in all the common organic solvents.

An aqueous solution of the diiodomaleic acid gave a white precipitate with silver nitrate, which exploded violently when heated in an air bath. A solution of the ammonium salt gave a white precipitate with lead acetate, but no action with a salt of calcium, strontium or barium.   ·

When a solution of diiodomaleic acid in either water or alcohol was treated with a drop of bromine water, no decoloration was observed. An aqueous solution of the acid decolorized potassium permanganate with precipitation of manganese dioxide, but nothing definite could be isolated from the product. Diiodomaleic acid was dissolved in alcohol and saturated with hydrochloric acid gas, the product was a brown liquid, which

[1] Salmony, Simonis. *Ber* , **38**, 2580 (1905)

could not be made to solidify, and was not studied further., Attempts to reduce the acid with sodium amalgam with water or alcohol, zinc or magnesium and sulfuric acid, or zinc dust and acetic acid, gave no results from which a definite compound could be isolated.

Diiodomaleic Anhydride.—Five grams of diiodomaleic acid were heated in 50 cc. of toluene until the solid had gone into solution. A few drops of a liquid separated, which was shown to be water by its action with dried copper sulfate. The yellow anhydride, obtained by evaporating off the solvent, after several crystallizations from naphtha, showed the constant m. p. $112-112.5°$ (uncor.), but analyses gave $1\,5\%$ to 1.9% too much iodine, and 1.5% to 1.4% too much carbon. A specimen of the anhydride, prepared by the action of acetyl chloride and a drop of sulfuric acid on the acid, gave 1.1% too much iodine, and after two more crystallizations, making 8 in all, 1.2% too much. It is evident, therefore, that our diiodo acid and anhydride contain a clinging impurity, which cannot be removed by crystallization, and this is confirmed by the fact that the constant melting point of our diiodomaleic anhydride, $112-112\,5°$ (uncor.) is $4°$ below that obtained by Diels and Reinbeck,[1] who made this substance by the action of sodium iodide on dibromomaleic anhydride in dry acetone. The properties of our substance are identical with those given by Diels and Reinbeck except that our preparation crystallizes in white prisms, which soon turn light yellow, while they describe theirs as yellow, and ours is soluble in benzene, theirs difficultly soluble. Although our analyses gave no satisfactory results, we were more successful with the determination of the molecular weight by freezing in benzene.

Calc for $C_2I_2(CO)_2O$ 350; found 312 5, 322 7, 316 6, 320 9

The anhydride is converted into the acid slowly by cold, quickly by hot water. That our substance was the diiodomaleic anhydride is proved, in spite of our bad results on the substance itself, by the analyses of its derivatives already given and by those that follow.

Acid Aniline Salt of Diiodomaleic Acid, $C_2I_2COOHCOOHNH_2C_6H_5$.—Two grams of diiodomaleic acid, dissolved in 150 cc. of ether, were treated with 4 cc. of aniline, and the white precipitate, after purification by washing with ether, was dried *in vacuo*.

Calc. for $C_2I_2COOHCOOHNH_2C_6H_5$: I, 55.07, found. I, 55.33, 55.58.

It decomposes at about $152°$, is soluble in water but insoluble in most of the common organic solvents. Its solution has an acid reaction to litmus, and is decomposed by sodium hydroxide with an odor of aniline. It is also decomposed if heated in an organic solvent.

Diiodomaleylphenylimide (Diiodomaleylanil), $C_2I_2(CO)_2NC_6H_5$.—The acid aniline diiodomaleate, described above, was made by adding a slight ex-

[1] *Ber.*, **43**, 1271 (1910).

cess of aniline to a solution of diiodomaleic acid in glacial acetic acid. The precipitate of the salt, which formed in a few minutes after being washed free from aniline with glacial acetic acid, was suspended in glacial acetic acid and heated on the sand bath, until it began to dissolve, when the lamp was removed and the flask allowed to stand on the hot sand till the solution was complete. The addition of a small quantity of water then threw down a yellow precipitate, which was crystallized from alcohol until it showed the constant m. p. 171–2° (uncor.).

Subst. 0.2502, AgI, 0 2758; Calc for $C_2I_2(CO)_2NC_6H_5$ I, 59 74, found I, 59 58

Properties of Diiodomaleylphenylimide.—Small, yellow prisms melting at 171–172° (uncor.); soluble in ether, chloroform, acetone, ethyl acetate, glacial acetic acid, benzene, toluene, nitrobenzene, or aniline; essentially insoluble in cold alcohol, or naphtha, soluble when hot. Strong hydrochloric acid produces no visible effect on it, even when hot; boiling alkali dissolves it slowly.

Further action of aniline converted the diiodo compound into phenylaminomaleylphenylimide[1] (anilinomaleylanil), which was also obtained when diiodomaleic acid was dissolved in alcohol, and treated with aniline in the proportion of 3 molecules to 1 of the acid; the mixture, disregarding the precipitate of the salt, was heated on the steam bath, which turned the liquid brown, and produced vapors of iodine. At the end of an hour the solution was allowed to cool, and the yellow product which separated was washed with cold alcohol and then crystallized from alcohol and later from benzene or toluene till it showed the m. p. 232–233° (uncor.).

Calc for $C_6H_5NHC_2H(CO)_2NC_6H_5$ C, 72 69, H, 4 58, N, 10 61, found C, 72 24, H, 4 54; N, 10 48

The substance can be prepared as well in a glacial acetic acid solution and is even formed when water is the solvent. Diiodomaleic anhydride also gave it when heated with aniline in absolute alcohol or glacial acetic acid.

In preparing the imide, occasionally a different product was obtained in small, yellow needles, melting at 261° (uncor.). It seemed to be phenylaminoiodomaleylphenylimide, but we did not have time to study it.

If the diiodomaleic acid was heated with *p*-toluidine and glacial acetic acid, the *p*-tolylaminomaleyl-*p*-tolylimide was formed, which was crystallized from alcohol till it melted constant at 229° (uncor.).

Calc. for $C_7H_7NHC_2H(CO)_2NC_7H_7$ N, 9 59, found N, 9 37

Action of Phenylhydrazine on Diiodomaleic Acid.—Three grams of diiodomaleic acid, dissolved in 50% alcohol, were treated with phenylhydra

¹ Reissert, Tiemann, *Ber*, **19**, 622; Reissert, *Ibid.*, p 1644 (1886); Michael, *Ibid.*, p. 1377; Wohl, Freund, *Ber*, **40**, 2300 (1907), Bischoff, Walden, *Ann.*, **279**, 140 (1894).

zine in the proportion of 3 molecules to 1.   After heating for 5 minutes on the steam bath, red needles separated, which were filtered out of the hot solution.   The filtrate, on cooling, deposited a few orange crystals, which were obtained in quantity by adding a little water to the solution. This is the principal product of the reaction, and it was purified by crystallization from 50% alcohol till it showed the constant m. p. 170° (uncor.), when it was dried *in vacuo*.

Subst 0.3172, 0 2262; N₂, 18 cc at 21° and 766 mm ; AgI, 0.2393; Calc for $C_2I_2(CO)_2NNHC_6H_5$: N, 6.37; I, 57 70; found: N, 6.67; I, 57 18.

The substance is therefore diiodomaleylphenylhydrazide.   The same substance was obtained from phenylhydrazine and diiodomaleic anhydride in absolute alcohol or glacial acetic acid.

Calc.. I, 57 70; found. I, 57.19

None of the red product was formed in this case.

Properties of Diiodomalcylphenylhydrazide.—It crystallizes in orange plates, which melt at 170° (uncor.) with decomposition and bubbling. It is soluble in alcohol, methyl alcohol, ether, chloroform, glacial acetic acid, benzene, toluene, nitrobenzene, or aniline; practically insoluble in carbon tetrachloride or naphtha.   Dilute acids have no apparent action even if hot; strong sulfuric acid dissolves it with a brownish red color; dilute alkali does not act on it in the cold but dissolves it on heating.

The red product also obtained by the action of phenylhydrazine on diiodomaleic acid, occurred in such small quantities that it could not be studied thoroughly.   The phenylhydrazomaleylphenylhydrazide would be expected, but our analyses do not accord well with this formula, and we could not get enough of it to repeat them.   It crystallizes in red needles, melting with decomposition at 226° (uncor.).   It is practically insoluble in the common organic solvents when cold; soluble in hot glacial acetic acid, benzene, or toluene.

Action of Water on Diiodomaleic Acid —Two grams of diiodomaleic acid were heated to 100° in a sealed tube with 30 cc. of water for 3 hrs.   Carbon dioxide was given off when the tube was opened; the other products were an aqueous solution and a brown oil.   The solution contained hydriodic acid and formaldehyde in large quantity, and a little free iodine. The oil, which contained a few white crystals, solidified on standing, and, after it had been pressed in filter paper, was separated by heating it with naphtha into a soluble and an insoluble substance.   As the work on these compounds was taken up at the end of the year, we have not been able to carry it beyond the preliminary stage.   The soluble compound was purified by crystallization from naphtha until it showed the m. p. 95–96° (uncor.), when it was dried *in vacuo*.

Subst. 0.1362, 0.1807; AgI, 0.2036, 0.2694; Calc. for CHI_2COOH: I, 81.40; found: I, 80.80, 80.59.

These analyses indicate that this product is diiodoacetic acid, but our substance is white and melts at 95–96°, whereas the diiodoacetic acid, according to Angeli,[1] is yellow and melts at 110°. The explanation of these discrepancies must be left to future work. Our product is soluble in water, giving an acid reaction, and decomposing carbonates. It is also soluble in alcohol, ether, or benzene; practically insoluble in cold naphtha, soluble in hot, from which it is deposited in rosets of white needles. On exposure to the air it turns pink, and gives a test for free iodine. With lead acetate it gives a white precipitate, which can be crystallized from hot water.

The compound insoluble in naphtha, when crystallized from glacial acetic acid, gave white plates contaminated with a small quantity of white prisms, but the latter were removed by warming gently with water, after which the plates were crystallized several times from glacial acetic acid.

Subst o 2492, AgI, o 4449, Calc for C_2HI_5, I, 96 23, found I, 96 49

The substance therefore seems to be pentaiodoethane, but it is unfortunate that we did not have time to prepare enough for another analysis. It forms white plates melting at 182–184° (uncor.) and is soluble in alcohol, glacial acetic acid, or benzene, and insoluble in naphtha.

CAMBRIDGE. MASS

THE SYNTHETIC PREPARATION OF dl-GLYCERIC ALDEHYDE.

BY EDGAR J WITZEMANN

The synthetic preparation of dl-glyceric aldehyde was accomplished by Wohl at least fifteen years ago.[2] Several workers have repeated the synthesis on a small scale since that time. In those instances in which crystalline glyceric aldehyde was obtained it was by the use of seed crystals obtained from Wohl. Others have been satisfied to work with the uncrystallized syrup. For some chemical work, such as that of Schmitz[3] on the mechanism of acrose formation, such syrups would be fairly satisfactory, but for certain biochemical as well as chemical work the pure crystalline compound is necessary, in order that the experimental results shall be sharply significant. As a part of the program of work on the metabolism of sugars, which is being followed in this laboratory, it became necessary to prepare a quantity of pure crystalline glyceric aldehyde for biochemical experiments. In the course of this work certain improvements were made in the method of preparation, especially in the manip-

[1] *Ber.*, **26**, 596 (1893).

[2] Wohl, *Ber*, **31**, 1797, 2394 (1898), Wohl and Neuberg, *Ber*, **33**, 3095 (1900).

[3] *Ber.*, **46**, 2327 (1913)

ulations of the highly sensitive glyceric aldehyde itself, which now make the isolation of the crystalline compound very certain and relatively easy. Glyceric aldehyde, as prepared by the use of these modifications, is much more easily crystallized than any known hexose including galactose.   In fact it has not been possible to prevent its spontaneous crystallization if care was used in the preparation of the syrup.

The actual work of preparation was done in the Kent Chemical Laboratory of the University of Chicago, through the kindness of Dr. J. U. Nef, and I hereby wish to thank him for this and for his helpful interest during the course of the work.

The method used by Wohl in the synthesis of glyceric aldehyde was followed carefully except that it was modified in some important details of manipulation.   Briefly summarized, this method is as follows: acrolein is dropped fairly slowly into twice its weight of absolute alcohol previously saturated at 0° with dry hydrochloric acid gas.

$$CH_2 : CHCHO + HCl + 2C_2H_5OH \longrightarrow CH_2ClCH_2CH(OC_2H_5)_2 + H_2O.$$
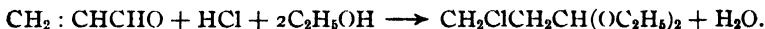
The β-chloropropionicaldehyde diethylacetal forms a separate lower layer which is separated, neutralized, etc., and finally treated with powdered sifted potassium hydroxide in order to convert it into acrolein diethylacetal.

$$CH_2ClCH_2CH(OC_2H_5)_2 + KOH \longrightarrow$$
$$CH_2 : CHCH(OC_2H_5)_2 + KCl + H_2O.$$
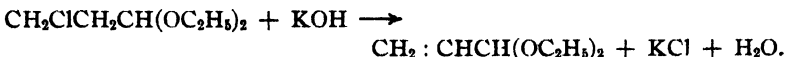
The acrolein acetal is oxidized with potassium permanganate to glyceric aldehyde diethylacetal.

$$3CH_2 : CHCH(OC_2H_5)_2 + 4H_2O + 2KMnO_4 \longrightarrow$$
$$3CH_2OHCHOHCH(OC_2H_5)_2 + 2KOH + 2MnO_2.$$
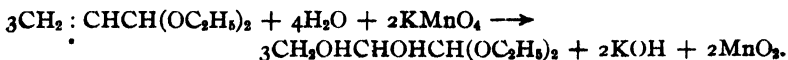
The glyceric aldehyde acetal in turn is hydrolyzed by 0.1 N sulfuric acid in the cold, and from this, finally, the true dimeric crystalline *dl*-glyceric aldehyde is obtained.

$$CH_2OHCHOHCH(OC_2H_5)_2 + H_2O \longrightarrow CH_2OHCHOHCHO + 2C_2H_5OH.$$

In the preparation of β-chloropropionicaldehyde diethylacetal, it was found best to add the acrolein[1] from a dropping funnel which passed through a cork fitted in the flask containing the absolute alcohol saturated with hydrochloric acid.   A small slit cut in the side of the stopper allowed the air to escape as fast as it was displaced by the acrolein.   A glass capillary tube in a cork was set into the top of the separatory funnel to prevent the acrolein vapors from passing out too freely.   The reaction mixture was constantly agitated in an ice bath during the addition of the acrolein.

[1] The acrolein used was obtained by the methods described in THIS JOURNAL, **36,** 1766 (1914)

If the acrolein was kept cooled in an ice bath and only added to the separatory funnel in relatively small amounts, this work could be done in the open room without causing any inconvenience or perceptible odor of acrolein.[1] The β-chloropropionicaldehyde acetal separates in part during the addition of acrolein. After standing an hour or so in the ice bath with occasional agitation, the lower layer was separated off. This was treated gradually with an excess of sodium bicarbonate according to the original suggestion of Wohl. The method of neutralizing the free hydrochloric acid with precipitated calcium carbonate[2] was not used. The voluminous precipitate of sodium chloride was filtered off under strong suction, pressed with a porcelain pestle and finally washed with a little absolute alcohol. The filtrate was washed several times with cold water, after which the β-chloropropionicaldehyde acetal was dried with potassium carbonate. In this condition it can be left over night. It is never advisable to keep the β-chloropropionic aldehyde acetal for long intervals. If it becomes necessary to keep it for a time it is not advisable to have it stand over moist potassium carbonate.

The crude β-chloropropionicaldehyde acetal thus obtained was always fractionally distilled *in vacuo*. The product distilling below 56° at 8 mm. pressure had a very powerful odor, probably due to β-chloropropionic aldehyde, which may arise either from the addition of hydrogen chloride to acrolein, which was not subsequently converted into the acetal, or it may arise from hydrolysis of the acetal. This fraction always gave an additional amount of the high boiling fraction on redistilling. The main fraction, distilling from 56–66° at 8 mm. was used at once for the preparation of acrolein acetal. The residue, on distillation, was a golden yellow liquid somewhat less viscous than glycerol. A portion of this residue was distilled *in vacuo*. Distillation took place all the way from 66° to 140° at 16 mm. (but most distilled at 120–40°). The first runnings were composed of β-chloropropionicaldehyde diethylacetal. On fractionating again a slightly yellow, nearly colorless, fraction, boiling at 127–40° at 10 mm., and having a mild odor resembling acrolein acetal was obtained. On attempting to remove this liquid with chromic acid cleaning mixture, a very large amount of acetaldehyde was evolved, showing that this distillate was composed in part of acetals. It was not further investigated.

Since no suitable copper still, such as was used by Wohl in the treatment

[1] This operation is very conveniently done in cold weather. The absolute alcohol saturated with HCl may be made up in quantity and kept for a long time by placing it in a strong bottle fitted with a rubber stopper. The bottle is set in a deep pan on the base of a strong ring stand and a ring is clamped down very firmly on the stopper. The whole is placed out of doors. If the temperature is above 0° the pan is filled with ice water a short time before removing the amount desired, otherwise not. In hot weather it is very troublesome to keep this solution.

[2] Wohl and Emmerich, *Ber.*, **33**, 2760 (1900).

of β-chloropropionicaldehyde acetal with potassium hydroxide was available, a 250 cc. round-bottomed flask was used   Fifty grams of β-chloropropionicaldehyde acetal were placed in the flask and 100 g. of powdered potassium hydroxide (passed through a 60-mesh sieve) were added a few grams at a time   Meanwhile, the contents of the flask were continually mixed by shaking. The flask was cooled in ice water from time to time. In this way a homogenous, cream-colored mixture was obtained.   The flask was then fitted with a cork containing a three-ball Glinsky distilling tube. The latter was connected with a short Liebig condenser. The flask was then immersed in a paraffin bath up to the level of the mixture inside. When the bath reached 210–20° an active reaction took place and acrolein diethylacetal began to pass over at once.   When the reaction proceeds quite normally, there was no difficulty in keeping the thermometer in the top of the Glinsky at or below 120°. The distilate was nearly always composed of two layers, the lower one of which was made up of a few drops of water. After removing the water with potassium carbonate the product was fractionated, using the Glinsky tube. Three portions of 50 g. thus gave an average of 80 g. of acrolein diethylacetal, distilling between 120–128° (95% of it between 123–5°).   This is 68% of that theoretically possible. There was always about 5–10 g. of ethyl alcohol formed by the saponification of one of the acetals. Likewise, a few grams of acrolein acetal may be recovered by digesting the flasks with water.   It was invariably noticed, on dissolving the potassium hydroxide residue, that there was a considerable amount of an insoluble substance floating in the solution of potassium hydroxide. The nature of this product was not determined. About 15% of the material used remained as a residue on fractionating the crude acrolein acetal. This sometimes gave satisfactory results on distilling again with powdered potassium hydroxide.

The formation of acrolein acetal from β-chloropropionicaldehyde acetal takes place with surprising ease and regularity when the powdered potassium hydroxide has the right qualities. If, however, a grade of potassium hydroxide is used which contains too much water, or if the grinding of the potassium hydroxide is done on a damp day, the results are regularly poor. It is very easy to determine, during the distillation, whether the results are going to be good. If the powdered potassium hydroxide melts before the acrolein acetal begins to distil over (105–20°), or if the distillation temperature remains at 78° (b. p. of alcohol), or if the distillate has an overpowering odor, (worse than acrolein) the reaction is not proceeding normally. Usually all three of these signs occur together. Sometimes, however, only the latter (that is the overpowering odor) is present to a slight extent. This is usually a warning that the yield will be a bit low and that more care should be taken to keep the potassium hydroxide dry.

The explanation of this undesirable result is not difficult. The reaction may be written thus:

$$
\begin{array}{ccc}
\text{CH}_2\text{Cl} & & \text{CH}_2\text{Cl}— \\
| & & | \\
\text{CH}_2 & + \text{H}_2\text{O} \longrightarrow & \text{CH}_2 + 2\text{C}_2\text{H}_5\text{OH} \\
| & & | \\
\text{CH}(\text{OC}_2\text{H}_5)_2 & & \text{CHO}
\end{array}
$$
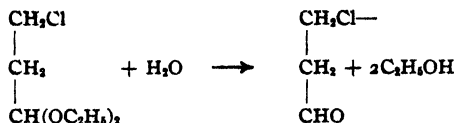
It is probable that only the β-chloropropionicaldehyde (the compound with the powerful odor) formed by the action of water vapor on the vapor of the acetal passes over into the distillate. The β-chloropropionicaldehyde formed by the action of water within the liquid mixture is no doubt polymerized instantly. This is shown by the fact that a white insoluble polymer appears in the distillation mass which increases in quantity as the reaction proceeds. Wohl and Emmerich[1] had similar trouble in hydrolyzing β-chloropropionicaldehyde acetal with aqueous potassium hydroxide in order to obtain β-hydroxypropionicaldehyde acetal.

After having gained sufficient experience with the technique, it was found possible to prepare, in about three weeks, enough acrolein (about 1600 g. from about 6000 g. of glycerol) and to convert this by successive stages into 735 g. of acrolein diethylacetal.

The oxidation of acrolein diethylacetal to glyceric aldehyde diethylacetal presents no difficulties, except that of getting a large yield. Wohl and Neuberg[2] succeeded in getting a maximum yield of about 40%. In my own experiments it was possible to get a maximum yield of 54%, not counting the unchanged acrolein acetal recovered, or an average of 52–53% for a series of oxidations. 540 cc. of water were placed in a three liter flask and 50 g. of acrolein acetal were added. To this 1100 cc. of an aqueous solution, containing 60 g. of potassium permanganate (i. e., nearly saturated at room temperature), were added from a dropping funnel at the rate of 100 cc. in five minutes. Throughout the addition, the mixture was vigorously agitated in an ice bath. The reaction mixture was then allowed to stand for 2 hours in the ice bath. Usually the entire contents of the flask set into a stiff jelly (i. e., of hydrated manganese dioxide hydrogel) in 15 to 30 minutes. This gel was so stiff that frequently the flask could be turned upside down without disturbing the gel. Gradually, if left undisturbed, this gel showed "condensation water" or syneresis and also deep fractures. After standing two hours it was placed on the steam bath. This hastens the further coagulation of the colloid, so that when the mixture has become fairly warm it may be thrown upon a large (8 inch) Buchner suction filter. By pressing the precipitate with a spatula the manganese dioxide may be sucked quite dry. It is then washed with about

[1] Ber., 33, 2760 (1900).
[2] Ibid, 33, 3095 (1900).

150 cc. of water. The warm filtrate (about 1800 cc.), which smells strongly of acrolein acetal, is treated with 900 g. of commercial potassium carbonate and the solution cooled at once. It is not necessary to add about 1800 g. of potassium carbonate as stated by Wohl. The mixture is now transferred to a large separatory funnel; the upper layer (glyceric aldehyde acetal) is drawn off and the aqueous solution extracted 4 or 5 times with ether. On mixing the ether extract with the crude acetal first drawn off, solution at first results; on addition of more ether, however, a considerable amount of glyceric aldehyde acetal separates out as a lower layer. This was discarded as water at first, but later its true nature was discovered. Experiments with pure glyceric aldehyde acetal and ether failed to show any such miscibility break in this binary system, so that the miscibility break observed here must be due to some third component, probably the water dissolved in the ether. At least it was found that the glyceric al dehyde acetal was taken up into solution again instantly as soon as potassium carbonate was added in order to dry the solution. After distilling off the ether, the crude glycericaldehyde acetal was distilled *in vacuo.* It boiled at 120–1° at 8 mm. pressure.

From 60 g. of acrolein acetal 39 to 40 g. of glyceric aldehyde acetal were nearly always obtained, and about 3 g. of unchanged acrolein acetal were recovered. From 835 g. of acrolein acetal 512 g. of pure glycericaldehyde acetal were obtained. Altogether, 1465 g. of acrolein acetal were worked up in this way.

dl-Glyceric Aldehyde.

In the preceding pages I have given some additional observations and details concerning the preliminary stages in the synthesis *dl*-glyceric aldehyde from acrolein and glycerol, but significant and important improvements were also made in the manipulation of the free glyceric aldehyde itself. Wohl apparently had considerable difficulty in crystallizing his glyceric aldehyde, and states that it required weeks to get the first crystals. Schmitz[1] found that very small concentrations of alkali condense glyceric aldehyde into a definite mixture of 2-keto-hexoses. Nef's long studies with the sugars[2] have shown how sensitive even the hexoses are to the action of inorganic bases and salts. In glyceric aldehyde all these properties would be even more marked. In view of these considerations, Nef suggested the use of small amounts of acetic acid to overcome the undesirable effects of any traces of alkali. The results obtained in the crystallization of glyceric aldehyde as a result of this suggestion are so remarkable in comparison with anything described in chemical literature that they will be described in some detail.

The glyceric aldehyde acetal was dissolved in 10 times its weight of

[1] *Ber.*, **46**, 2327 (1913).
[2] *Ann.*, **357**, 214–312 (1907); **376**, 1–119 (1910); **403**, 204–383 (1914).

0.1 N sulfuric acid and allowed to stand at room temperature for a few days, or better for a whole week. To this was added 6.3 g. of glacial acetic acid per 100 cc. The solution was then warmed and slightly more than the calculated quantity of barium hydroxide (about 0.3 N) was added a little at a time.[1]

The solution was filtered after standing for some time to remove as much of the barium sulfate as possible (*i. e.*, all but at most a slight turbidity). Test portions were placed in test tubes and a small amount of the 0.1 N sulfuric acid was added to one of them. Both were warmed somewhat and the turbidities were compared. The solution was adjusted by the addition of small amounts of sulfuric acid until it showed only a very slight positive test for barium as shown by the formation of a slight turbidity on adding a little 0.1 N sulfuric acid to a test portion.

This solution was then filtered through a hard filter containing a pinch of animal charcoal and the water was then removed from the clear, colorless, filtrate by distillation at 20 mm. pressure. The syrup remaining was dissolved in the minimal amount of warm absolute alcohol and an equal volume of ether added (*i. e.*, until a turbidity begins to appear). On standing for 25 hours the last traces of inorganic matter were separated out and the clear filtrate then gave, on customary distillation at reduced pressure, a transparent syrup; this syrup was now transferred to a beaker and placed in a vacuum desiccator over night. The next morning the syrup showed a white opalescence. Before night the syrup had become white and opaque. A little ethyl alcohol was now stirred into the mass from time to time until the mass ceased to be sticky any longer. Thirty grams of glyceric aldehyde acetal treated in this way gave, in three days, 10 g. of a crystalline powder nearly insoluble in cold ethyl alcohol, with which it was freely washed on a filter. The glyceric aldehyde thus obtained melts 132° without further purification. This was the only experiment in which the passage of glyceric aldehyde through the colloidal state, was so clearly noticed. In all subsequent experiments more dilute syrups were used for crystallization in order to obtain larger crystals.

After a few more batches of glyceric aldehyde had been worked up in this way and inocculated with particles of the above crystals, it became evident that the yield in crystalline glyceric aldehyde was considerably less than the amount theoretically possible from the acetal used. This may have been due to unhydrolyzed acetal or to some condensation of rearrangement product of the glyceric aldehyde itself. The following procedure was therefore adopted:

The acetal was hydrolyzed for a week at room temperature just as

[1] The method used by Wohl at this point was to simply neutralize the sulfuric by adding an excess of barium hydroxide and then to remove the excess of barium hydroxide at once by passing a stream of carbon dioxide through the solution.

before, except that it was twice warmed for about 2 hrs. to about 35° during the hydrolysis. Before adding the barium hydroxide, 0.5 g. of glacial acetic acid was added per 100 cc., of the solution. The end adjustment of the trace of barium acetate was made as before. The final removal of the last portions of barium sulfate was accomplished by filtering through a hard filter containing a pinch of animal charcoal, which had been washed thoroughly with hydrochloric acid and then with water till free from acid. The solution was now concentrated *in vacuo* to a thick syrup free from water. This was dissolved in absolute alcohol. When prepared in this way it is impossible to prevent spontaneous crystallization of alcohol solutions of the glyceric aldehyde. This solution is treated with ether, filtered and concentrated *in vacuo* at once. If it is to be transferred from the distilling flask it must be done quickly, because in twenty minutes after the removal of the water bath crystallization is well advanced. In fact, in a few cases, crystallization began while the flask was being heated. In twenty-four to forty-eight hours crystallization is complete.

When crystallization is complete the flask usually contains a thick, porous cake of crystals covered with a layer of limpid mother liquor a few millimeters thick. The cake is broken up and thrown on a suction filter. The flask and crystals are repeatedly washed with absolute alcohol after which the crystals are spread out on a porous plate and allowed to dry After standing in the air one day the melting point was found to be 142°. The highest melting point previously observed (138°) was obtained by Wohl and Neuberg[1] after recrystallizing their product from 40% methyl alcohol and drying *in vacuo* over phosphorus pentoxide. A specimen kept in a vacuum desiccator over concentrated sulfuric acid for three days melted at the same temperature, thus showing that this sugar is not hygroscopic. The glyceric aldehyde syrup is quite sweet. Wohl states that the crystals are less sweet than the syrup. This is true. In fact, there is no perceptible taste whatever when crystals are placed on the tongue and allowed to dissolve there.

The mother liquor was concentrated *in vacuo* and allowed to crystallize again.

The behavior of *dl*-glyceric aldehyde in crystallization is very interesting. As was shown above, much better results in crystallization are obtained when inorganic compounds present in the small amount of bone-black used are kept out of the solution. Just what the effect of these salts ($Ca_2P_2O_7$, $CaCO_3$, etc.) is, has not as yet been determined experimentally. Furthermore, success in crystallization depends in part on the complete removal of water from the syrup. If the water has been completely removed and the syrup taken up in alcohol, the crystalline dimeric form (since this is almost insoluble in alcohol) begins to separate out at once.

[1] *Ber.*, **33**, 3095 (1900).

The addition of ether to the alcohol solution does not interfere with crystallization. In fact, considerable crystalline glyceric aldehyde was obtained from this mixed solvent. But even with the technique described, the results obtained in crystallization are somewhat variable, as will be seen from the results given below. Moreover, no experimental explanation has yet been found for the fact that usually only 75% of the glyceric aldehyde theoretically possible could be crystallized out of any given batch.

In some test experiments the following results were obtained: Ninety grams of the acetal gave, on the first crystallization, 28.5 g. of glyceric aldehyde crystals. On concentrating the mother liquor and washings *in vacuo* a second crop of 8.2 g. was obtained. The washings from the second crop gave 11.0 g. of gum which no longer crystallized on diluting with alcohol. Therefore, 75% of the 49.3 g. of glyceric aldehyde theoretically possible were obtained in the crystalline form.

In another experiment, 27 g. of crystalline glyceric aldehyde out of the 41.7 g. theoretically possible were obtained from the first crystallization, *i. e.*, 64.7%. A second crop of 4.7 g., and a third crop of 3.7 g. was obtained, making a total of 84.8% recovered as crystals.

Altogether, enough material was worked up to have given 400 g. of crystalline glyceric aldehyde, assuming that 95% of it could be crystallized. As a matter of fact, only a little over 250 g. was obtained altogether.

CHICAGO, ILL.

A FURTHER STUDY OF THE PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF ORGANIC ACIDS. FOURTH COMMUNICATION.[1]

BY LeRoy McMaster

In continuation of the investigation of the preparation and properties of the neutral ammonium salts of organic acids, I still find that the salts were always prepared by neutralizing an aqueous solution of the organic acid with ammonia water or ammonium carbonate, and the solution allowed to evaporate. As a result, the acid salts, instead of the neutral salts, were generally obtained, due to the hydrolytic action of water upon them. The properties given are thus the properties of the acid salts. In some cases no record at all can be found of the preparation of any ammonium salt of the organic acid. Many of the salts also contained water of crystallization.

In attempting to prepare some neutral di-ammonium salts by the above

[1] For previous papers on this subject see· *Am. Chem. J*, **49**, 84–87 (1913); *Chem. News*, **108**, 136–137 (1913); *Am. Chem. J.*, **49**, 294–301 (1913); *Chem. News*, **108**, 182–183, 193–194 (1913); THIS JOURNAL, **36**, 742–747 (1914).

general method, Keiser and McMaster[1] always obtained the acid salts. They then dissolved the organic acids in absolute ethyl alcohol or ether and conducted a stream of dry ammonia gas into the solution.   By this method they were thus able to prepare neutral di-ammonium salts of several of the organic acids.   I[2] continued the preparation of neutral ammonium salts in methyl alcohol, ethyl alcohol and ether and studied their properties, many of which were found to be different from those described in the literature.   There have been prepared by this method, in this laboratory, the neutral ammonium salts of propionic, butyric, isobutyric, isovalerianic, caproic, malonic, succinic, glutaric, ethyl malonic, adipic, pimelic, sebacic, fumaric, maleic, itaconic, citraconic, mesaconic, tartronic, malic, tartaric, racemic, crotonic, benzoic, cinnamic, o-phthalic and m-phthalic acids.

The work on the preparation of neutral ammonium salts of organic acids and a study of their properties has been continued.   There have been prepared and studied the neutral ammonium salts of palmitic, stearic, oleic, elaidic, aconitic, salicylic, m-hydroxy benzoic, p-hydroxybenzoic, p-methoxybenzoic, hydrocinnamic, hippuric, o-toluic, phenyl acetic, mandelic and uvitic acids.   They were prepared in absolute alco alcohol and ether.   Several were prepared also in acetone.

Some of the ammonium salts of the organic acids are more or less soluble in alcohol, and, when such was found to be the case, they were generally precipitated from a saturated solution.   Before filtering, ether was generally added to decrease their solubility.   As a rule, the salts were generally precipitated in a crystalline form from the alcoholic solution and in an amorphous condition from the ethereal solution.   On passing ammonia into the solutions, there are frequently formed at first gelatinous or mucilaginous precipitates which generally change in a short time to crystalline or amorphous powders.   This happens more frequently in the ethereal solution than in the alcoholic.   In the acetone solutions so far studied, granular powders are formed at once on passing in the ammonia.

In the following work the neutral ammonium salts of palmitic, stearic, oleic and elaidic acids were prepared and analyzed by Mr. John D. Fleming, Jr.   The ammonium salicylate and hippurate were also analyzed by Mr. Fleming, to whom I desire to express my sincere thanks.

Of the Higher Fatty Acids.

Ammonium Palmitate.—On attempting to prepare the neutral ammonium salt of palmitic acid by treating the acid with ammonia, Fremy[3] obtained the acid salt, insoluble in cold water.   The neutral salt can be readily

[1] Keiser and McMaster, *Am Chem. J* , **49**, 84 (1913).

[2] *Loc cit.*

[3] Fremy, *Ann* , **36**, 46 (1840)

prepared by passing dry ammonia gas into an ethereal solution of the acid, when it is formed as a very voluminous, white gelatinous precipitate. It does not become crystalline even after passing in the gas for three hours. This precipitate was first filtered by suction, washed with ether and dried in the air. Prepared in this manner, it lost ammonia and turned to a yellow curdy substance resembling a "soap." The freshly precipitated substance was next quickly filtered by suction on an alundum crucible, placed in a glass tube and a current of dry ammonia conducted over it to remove the ether. It was then placed for a few minutes in a vacuum desiccator and analyzed. Determination of the nitrogen by the Kjeldahl method proved it to have the composition of the neutral salt.

Calc for $C_{16}H_{31}O_2(NH_4)$ 5 13%; found· 5 16% N

The neutral salt when first precipitated is white, but soon becomes somewhat yellow. It is not hygroscopic, but loses ammonia, especially in moist air. It is slightly soluble in ether and petroleum ether, readily soluble in methyl alcohol, ethyl alcohol and acetone, and insoluble in carbon tetrachloride and benzene. There is considerable frothing when the salt is shaken with water.

Palmitic acid was also dissolved in ethyl alcohol and the solution treated with ammonia gas. After a short time, a crystalline precipitate was formed which went into solution upon the addition of a small amount of alcohol. The solution was poured into a crystallizing dish and the alcohol allowed to evaporate. The salt obtained was at first pure white, but before the evaporation was complete it became yellowish. After the alcohol had entirely evaporated and the salt became dry, it had the appearance of the compound prepared in ether. It had lost ammonia and analysis proved it to be the acid salt. In order to obtain neutral ammonium palmitate it was thus very evident that the salt must not be exposed to the air for any length of time. The compound prepared in either alcohol or ether is evidently an ammonium "soap."

Ammonium Stearate.—Stearic acid was dissolved in ether and dry ammonia conducted into the solution. A white gelatinous precipitate was formed which, after a short time, appeared to be somewhat crystalline. Like the palmitate, this salt loses ammonia in ordinary air, and it was necessary to filter it very quickly by suction and dry it in a current of ammonia gas. The salt thus prepared is not hygroscopic, is stable in dry air, but loses ammonia in moist air. It is practically insoluble in ether, benzene, carbon tetrachloride and petroleum ether, but very soluble in methyl alcohol, ethyl alcohol and acetone. It froths considerably when shaken with water. When an alcoholic solution of the acid is saturated with ammonia gas and the mixture allowed to evaporate in the air, there is obtained a soapy residue which analysis shows to be an acid salt instead of the neutral salt. This is due to the fact that it has lost ammonia

during the evaporation of the alcohol   When a small amount of the neutral salt prepared in ether was dissolved in alcohol, and the alcohol quickly evaporated, the residue was partly amorphous and partly made up of needle-like crystals   We have with the stearate another example of an ammonium soap

Determinations of the nitrogen by the Kjeldahl method gave results slightly higher than the calculated amount for the neutral salt   This may have been caused by a small amount of free ammonia not being removed, although the salt was placed over sulfuric acid in a vacuum desiccator

<div align="center">Calc for $C_{18}H_{35}O_2(NH_4)$ 4 65% found   4 80 and 4 81% N</div>

Ammonium Oleate —For the preparation of liquid-crystalline ammonium oleate, Lehmann[1] has made the neutral anhydrous ammonium oleate by passing ammonia gas from a steel cylinder into oleic acid until it smells strongly of ammonia   If this preparation is fused under a cover-glass on a slide, and "the cooling is watched under a microscope, it is seen that the mass solidifies as a whole to small needle-shaped (rhombic?) crystals of a labile modification   These are soon converted into a rather less fusible stable modification appearing as imperfectly formed (monoclinic?) leaflets   From alcoholic solution these latter can be obtained as relatively large crystals with sharp edges "   Lehmann also states that an anhydrous acid ammonium oleate does not exist and that solid neutral ammonium oleate dissolves in oleic acid from which it crystallizes out again unchanged   The neutral anhydrous ammonium oleate can also be prepared by conducting dry ammonia gas into an ethereal solution of oleic acid   At first there is formed a white gelatinous precipitate which becomes somewhat crystalline after running in the gas about one hour It is impossible to filter the mixture even by suction   The ether was removed by a current of dry ammonia gas and the salt finally dried in a stream of dry air   It is very deliquescent and loses ammonia easily in moist air   When shaken with water it forms a milky suspension

<div align="center">Calc for $C_{18}H_{33}O_2(NH_4)$ 4 68%   found   4 67% N</div>

When it was found that the ether could not be removed by filtration from the precipitated salt, the mixture was poured into a crystallizing dish When the ether had evaporated, there remained a very viscous liquid which on stirring became semi solid   During the evaporation of the ether, moisture was taken up by the gelatinous precipitate and there was presumably formed neutral ammonium oleate hydrate   This is practically what was observed by Lehmann[2] in the preparation of liquid crystalline ammonium oleate— 'If we continue to add water to the solid anhydrous

[1] *Sitz b Heidelberger Akad Wiss* **1913**, A xiii *Chem News* **108**, 191 1913)
[2] *Loc cit*

crystals of ammonium oleate it may easily be seen under the microscope that when the amount of water has reached a certain definite limit, the whole mass is converted into the syrupy liquid-crystalline modification. Thence forward no needles or leaflets of the anhydrous modification appear; the mass has become neutral ammonium oleate hydrate." That the mass referred to above will take up moisture readily was also noted by Lehmann for—"it is sufficient to leave the preparation uncovered for some time, when it absorbs moisture from the air, or to breathe on it."

Ammonium Elaidate.—No record can be found of the preparation of this salt. Elaidic acid was dissolved in ether, and ammonia passed into the solution. A glistening, white, gelatinous precipitate was formed which was filtered, washed with ether, and dried in a current of dry air. When thus dried, it became an amorphous soap-like substance. Ammonium elaidate can also be prepared in alcohol by saturating an alcoholic solution of the acid with ammonia gas and allowing the alcohol to evaporate. Since this salt loses ammonia slowly in the air, it is better to pass the ammonia gas into a saturated alcoholic solution of the acid, when white, translucent crystals are precipitated at once. These can be filtered, washed with ether, and dried in a desiccator. White, crystalline flakes are thus formed. The salt prepared in either medium is not deliquescent. The salt is soluble in methyl alcohol, ethyl alcohol, acetic acid and acetone. Analysis of the salt prepared in ether showed it to be the neutral ammonium elaidate.

Calc. for $C_{18}H_{33}O_2(NH_4)$: 4.68%; found: 4.61% N.

Of a Tribasic Acid.

All the previous preparations have been the neutral salts of monobasic and dibasic acids. The method having proved so very applicable in these cases, it was tried on the preparation of a neutral ammonium salt of a tribasic acid. Neutral ammonium aconitate was prepared, but only with difficulty, on account of it being so very deliquescent and losing part of its ammonia so readily. It suffices to show that the method is of very general application.

Ammonium Aconitate.—Several attempts were made to prepare the neutral ammonium salt of aconitic acid. When ammonia is passed into a solution of the acid in ether or in methyl alcohol, a mucilaginous precipitate is formed. This will not crystallize, even if the ammonia is conducted into the ethereal or alcoholic solution for a long time. A white colloidal precipitate is formed if the ammonia is passed into a solution of the acid in ethyl alcohol. After standing four days, this precipitate settled out mostly as an amorphous powder, but a small part of it was gummy. It was not analyzed. Baup[1] has also found that the neutral ammonium

[1] Baup, *Ann.*, **77**, 302 (1851).

salt of aconitic acid will not crystallize. The salt was prepared by Baup in aqueous solution and allowing the solution to evaporate to crystallization. .

Ammonia was then passed into a saturated alcoholic solution of the acid to which a small amount of ether was added. A granular precipitate was now formed. This was quickly filtered by suction, washed with ether, and placed over sulfuric acid in a vacuum desiccator for a short time. Analysis of two samples of the salt thus prepared gave, respectively, 16.08% and 16.09% of nitrogen. The neutral salt of aconitic acid contains 18.67% nitrogen. Since this salt is very deliquescent and readily loses ammonia, it was again prepared as just described and placed in a desiccator containing sodium hydroxide instead of sulfuric acid. Two analyses of this salt gave, respectively, 18.63% and 18.65% nitrogen, showing that it was the neutral compound. This salt gave a neutral solution when dissolved in water, in which it is very soluble, but soon hydrolyzes. It is soluble in acetic acid, slightly soluble in methyl and ethyl alcohols and insoluble in ether.

Of the Hydroxy-Benzoic Acids.

Ammonium Salicylate.--Cahours[1] prepared the normal salt of salicylic acid by evaporating a hot, concentrated solution of salicylic acid and ammonia water. Upon cooling, the ammonium salt crystallized out in scales. A dilute solution produced, by slow evaporation, glittering, silky crystals, which, dried in the air, had the composition $NH_4C_7H_5O_3$. The salt was found to be very soluble in water; by dry distillation, it decomposed into water and the amide of salicylic acid. Marignac[2] obtained this salt as monoclinic crystals containing 0.5 molecule of water of crystallization.

When ammonia gas was passed into an ethereal solution of salicylic acid, white, pearly scales were formed. An aqueous solution of the salt was neutral and produced, with ferric chloride, a wine-red color. It is not deliquescent, and loses ammonia only in moist air. It is very soluble in water, methyl alcohol, ethyl alcohol and acetic acid.

Calc. for $C_7H_5O_3(NH_4)$: 9.03%; found. 9.04% N

Ammonium-m-Hydroxybenzoate.—The ammonium salt of *m*-hydroxybenzoic acid was first prepared by Barth[3] by dissolving the acid in dilute ammonia water and allowing the solution to evaporate. The salt crystallized in needles in fascicular aggregates and was found to be very soluble in water. It contained no water of crystallization, and lost ammonia if dried on the water-bath. Analysis of the air-dried salt showed it to have the formula $C_7H_5O_3NH_4$.

[1] Cahours, *Ann.*, **52**, 336 (1844).
[2] Marignac, *Jahresb. Fortschritte Chem.*, **1855**, p. 485.
[3] Barth, *Ann.*, **148**, 36 (1868).

When ammonia gas is passed into an ethereal solution of m-hydroxy-benzoic acid until a portion of the salt, on being dissolved in water, shows a neutral solution, there is formed a white, granular precipitate of neutral ammonium m-hydroxybenzoate. When the ammonia is first passed in, the precipitate formed is very mucilaginous. The salt was washed with ether and dried in the vacuum desiccator. It is not deliquescent. In dry air the salt is stable, but loses ammonia in moist air. It is soluble in methyl alcohol, ethyl alcohol and acetic acid. It gives no color with ferric chloride. The salt crystallizes from ethyl alcohol in needles.

This salt can also be precipitated in acetone, in which it is but slightly soluble. When the ammonia is passed into the solution of the acid in acetone, no mucilaginous precipitate is formed at first, as in the case of the ethereal solution, but a granular powder is formed at once. The salt prepared in either acetone or ether slowly hydrolyzes when dissolved in water.

Prepared in ether Calc for $C_7H_5O_3(NH_4)$: 9.03%, found. 9 05% N   Prepared in acetone Found: 9 02% N

Ammonium p-Hydroxybenzoate.—This salt has been prepared by neutralizing the aqueous solution of p-hydroxybenzoic acid with ammonia water and the solution allowed to evaporate. It crystallized out from solution in long prisms and contained one molecule of water of crystallization.

This salt can also be prepared by passing dry ammonia gas into a saturated alcoholic, an ethereal, or an acetone solution of the anhydrous acid. In the alcoholic solution fine needle-like crystals are formed, in the ethereal solution a gelatinous precipitate is first formed which turns to an amorphous powder, while an amorphous powder is formed at once in the acetone solution. The salt was filtered by suction and washed with ether in each case. It is not deliquescent and imparts a neutral reaction to water, in which it is very soluble. It slowly hydrolyzes when dissolved in water. The aqueous solution gives no color with ferric chloride. It loses ammonia in moist air. The salt is readily soluble in methyl alcohol and acetic acid, very slightly soluble in acetone and appreciably so in ethyl alcohol. It is insoluble in ether. Analysis was made of the salt prepared in ether.

Calc. for $C_7H_5O_3(NH_4)$: 9.03%; found: 9 05% N.

Ammonium p-Methoxybenzoate.—The ammonium salt of p-methoxy-benzoic acid (anisic acid) is described by Laurent[1] to be rhombic plates of the composition $NH_4C_8H_7O_3$. When ammonia was passed into a solution of the acid in alcohol, pearly white crystalline leaflets were formed, which were filtered, washed with ether and dried in a vacuum desiccator. The salt is stable in the air, and an aqueous solution of it is neutral to sensitive litmus paper. It is not deliquescent and its aqueous solution

[1] Laurent, *Berz Jahrb.*, **23**, 415.

does not hydrolyze. It is readily soluble in methyl alcohol and acetic acid, and appreciably so in ethyl alcohol and acetone. A white, curdy precipitate, soluble in ammonia water, is formed when silver nitrate is added to an aqueous solution of the salt.

<div style="text-align:center">Calc. for $C_8H_7O_3(NH_4)$: 8 29%; found. 8 31% N</div>

When ammonia gas was conducted into an ethereal solution of p-methoxybenzoic acid, there was first formed a gelatinous precipitate which changed to a fine, crystalline powder. It can be crystallized from acetone in the form of fine feather-like needles.

Of Some Other Aromatic Acids.

Ammonium Hydrocinnamate.– Beilstein[1] describes this salt as small leaflets, easily soluble in water and readily losing ammonia. When ammonia is run into an ethereal solution of hydrocinnamic acid there is formed a white, gelatinous precipitate, which on drying changes to white, lustrous leaflets. The salt thus formed is the neutral ammonium hydrocinnamate, soluble in water, methyl alcohol, ethyl alcohol and acetic acid. It is insoluble in ether. The salt is slightly hygroscopic and loses ammonia in the air. Ferric chloride forms a yellowish precipitate with an aquesous solution of it.

<div style="text-align:center">Calc for $C_9H_9O_2(NH_4)$ · 8 38%; found 8 37% N</div>

On account of the great solubility of this salt in ethyl alcohol, it cannot be precipitated in this medium. Ammonia was run into a solution of 2 g. of the acid in ethyl alcohol for one hour, the alcoholic solution poured into a crystallizing dish and allowed to evaporate in the air over night. A heavy oily substance remained instead of the pure salt. This oil was acid to litmus paper. On distilling it, ammonia was first evolved, then fumes which condensed to a white solid. The mercury of the thermometer then rose to 260° and a heavy, refractive oil passed over which redistilled at 245° (uncor.). Hydrocinnamic acid[2] is easily changed partly into its ethyl ester of boiling point 247° (cor.) by merely dissolving it in ethyl alcohol. On the other hand, the ester just as readily changes back to the acid by the moisture of the air. Ethyl hydrocinnamate is also very refractive. The oily residue which was obtained above by allowing the alcoholic ammonia solution of hydrocinnamic acid to evaporate in the air was thus a mixture of hydrocinnamic acid, its ammonium salt, and its ethyl ester.

Ammonium Hippurate.– A salt of the formula $NH_4C_9H_8NO_3.C_9H_9NO_3 + H_2O$ was obtained by Schwarz[3] by treating hippuric acid with an excess of ammonia. He was unable to prepare the neutral salt, and no record of its preparation can be found. When ammonia gas was run into a satura-

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[1] Gjacosa, Hoppe-Seyler's, *Z physiol Chem*, **8**, 109 (1883)

[2] Erlenmeyer, *Ann.*, **137**, 330 (1866).

[3] Schwarz, *Ann.*, **54**, 37 (1845).

ted alcoholic solution of hippuric acid to which was added a small amount of ether, glistening, pearly, white laminae were formed These were filtered on an alundum crucible and washed with ether The salt is stable in dry air but loses ammonia slowly in moist air It is not deliquescent, and an aqueous solution of it is neutral It is soluble in methyl alcohol and ethyl alcohol It is somewhat soluble in acetone, from which it crys tallizes in beautiful needles It is insoluble in ether

Determination of the total nitrogen by the Kjeldahl method proved it to have the composition of the neutral salt .

Calc for $C_9H_8NO_3(NH_4)$ 14 29% found 14 30% N

Ammonium o-Toluate —This salt cannot be precipitated by passing ammonia into an alcoholic solution of the acid on account of its great solubility in the alcohol When the solution is evaporated, crystalline needles are formed A fine, white, crystalline precipitate is formed if the gas is passed into an ethereal solution of the acid The salt is not deliquescent but is readily soluble in water, giving a neutral solution The salt is stable in dry air, but loses ammonia slowly in moist air It is soluble in methyl alcohol, ethyl alcohol, acetic acid and acetone

Calc for $C_8H_7O_2(NH_4)$ 9 15% found 9 15% N

Although some of the salts of *o* toluic acid have been prepared and studied, no mention of the neutral ammonium salt can be found

Ammonium Phenylacetate —This salt was prepared by Moller and Strecker[1] by dissolving the acid in ammonia water and allowing the solution to evaporate to crystallization The salt was obtained only with difficulty on account of its great solubility Fine, white needles are formed if ammonia gas is conducted into a saturated alcoholic solution of phenyl acetic acid, while a fine, white, semi crystalline precipitate is formed, if the ammonia is run into an ethereal solution of the acid Before filtering off the crystals formed in the alcoholic solution it is necessary to add ether, for they are quite soluble in the alcohol The salt is fairly stable in the air, losing its ammonia but slowly in moist air The salt does not deliquesce, and imparts a neutral reaction to a water solution of it It is very soluble in water methyl alcohol and acetic acid, but only slightly so in acetone

Prepared in alcohol Calc for $C_8H_7O_2(NH_4)$ 9 15% found 9 12% N Prepared in ether Found 9 15% N

Ammonium Mandelate —This salt was first prepared by Winckler[2] by treating an aqueous solution of mandelic acid with ammonia water and allowing the solution to evaporate slowly The ammonium salt crystallized out only with difficulty as a yellowish white, soft mass, ex-

[1] Moller and Strecker *Ann* 113, 66 (1860)
[2] Winckler *Ann* 18, 317 (1836)

tremely soluble in water and in alcohol Duparc and Pearce[1] prepared the salt in the form of rhombic prisms

The neutral ammonium salt of mandelic acid was prepared by the usual method in ether When the ammonia was added there was first formed a white mucilaginous precipitate which soon changed to a fine crystalline powder, very soluble in water, methyl alcohol, ethyl alcohol and acetic acid, but insoluble in ether and acetone The salt, being very deliquescent in the air, was quickly filtered, washed with ether, and dried for a short time over sulfuric acid in a vacuum desiccator It gave a neutral solu tion when dissolved in water It loses ammonia in moist air The salt can be crystallized from ethyl alcohol in aggregates of fine needles

Calc for C_8H_7O (NH_4) 8 28% found 8 29% N

Ammonium Uvitate —No record can be found of the preparation and properties of this salt other than being mentioned by Finck[2] that it is im possible to precipitate it out of its aqueous solution by alcohol When dry ammonia gas was run into an alcoholic solution of uvitic acid, no pre cipitate was formed Upon the addition of ether to this solution a white, flocculent precipitate was formed This was filtered by suction, keeping the alundum crucible filled with ether to prevent the salt going into solu tion on account of the alcohol present The salt dried in a vacuum desiccator to an amorphous powder It is readily soluble in water to which it imparts a neutral reaction It is soluble in methyl alcohol, ethyl alcohol, and acetic acid, slightly soluble in acetone and insoluble in ether The salt is not deliquescent The salt prepared in ether had these same properties, and analysis showed it to be the neutral ammonium salt of uvitic acid

Calc for $C_9H_8O_4(NH_4)_2$ 13 08% found 13 10% N

This investigation is being continued with other organic acid especially the substituted acids

St Louis Mo

SOME NATURAL INDICATORS.
By H W BRUBAKER

Cohn, in his ' Indicators and Test Papers," states that the coloring matter from roses (*Rosa Gallica*) gives a deep red with green fluorescence in alkalies and light red in acids I found that the coloring matter from *Rosa rugosa* gives a green color in alkalies, red in acids and coloress be tween these two The coloring matter was extracted by triturating the petals in a mortar with some sea sand and 95% alcohol This was then filtered and the filtrate evaporated to dryness somewhat above room tem-

[1] Duparc and Pearce *Z Kryst Min* **27**, 611
[2] Finck *Ann* **122**, 186 (1862)

perature. Upon taking the red coloring matter up in water, most of the fatty substances were left undissolved. This water extract was of a very bright red color. To preserve the solution, enough alcohol was added to make a 50% alcoholic solution. The addition of the alcohol partly decolorized the solution. This solution, when used as an indicator, was changed to green by 0.1 N NaOH and, upon titrating with 0.1 N HCl, went through a blue green to colorless and then to pink in the acid solution. The neutral point was coincident with the colorless point which was changed to either green or pink by 1 drop of 0.1 N NaOH or, 0.1 N HCl, respectively. The fact that the neutral point is colorless is probably due to the mutual destruction of the coming pink by the going green or *vice versa*.

Upon titrating a 0.2 g. sample of sodium bicarbonate with 0.1 N hydrochloric acid, using methyl orange as the indicator, there were required 24.8 cc. of the acid. Upon repeating the titration, using the rose extract as indicator, the correct end point was not recorded unless the solution was boiled to drive off the carbon dioxide, in which case exactly the same amount (24 8 cc.) of the acid was required to give the colorless point. This indicator, therefore, behaves like phenolphthalein toward carbon dioxide. It is a weak acid substance. Rose test paper, made by dipping filter paper into the solution and drying, changed from green in alkalies to red in acids. It was found to be sensitive to 1 part of NaOH in 25,000 parts of water. The extracted coloring matter from several other species of roses behaved, in general, like the one described above.

The coloring matter from the Perennial Pea (*Lathyrus Latifolius* L) behaved in a manner similar to that from the rose, giving a green color in alkalies red in acids and colorless at the neutral point. This substance, when extracted from the blossoms with 95% alcohol, gave a nearly colorless solution, which acquired a slight pink color on standing and which developed color very sharply in either acids or alkalies.

The coloring matter from the Iris (Blue flag), extracted as described above with alcohol and evaporated to dryness, gave a purple substance which was taken up in water to separate it from fatty substances. This coloring matter changed to green in alkalies and red in acids and, like the rose color, gave a colorless solution at the neutral point. The alcoholic extract obtained from the purple Vetch gave the same color changes. The principal coloring substance of each of the above flowers seems to be the same, or very closely related chemically, as it behaves, in general, the same in all cases toward acids and alkalies. It is probably the same substance as found in the hollyhocks and dahlia, which is described by Cohn. If the original alcoholic extract of certain varieties of roses is evaporated on a water bath, glucosides present decompose, giving rise to a large amount of caramel which obscures the natural red coloring

matter   The petals of most flowers, especially the blue, red, pink, purple, etc , ones change color when placed in alkaline solutions and back to the original color or to some shade of red when placed in acids

The following table gives a list of some changes noted

I lower	In NH₄OH	In HCl
Crimson geranium	dark purple	bright red
Orange red geranium	bright purple	orange red
Martha Washington geranium	blue to greenish blue	red
White geranium	yellow	white
Mock orange (white)	yellow	white
White pansy	canary yellow	white
Purple pansy	greenish blue	red
Dark red pansy	dark blue green (almost black)	red
Yellow pansy	no effect	no effect
Yellow and brownish red colors mixed pansy	the yellow unchanged / the brownish red changed / to dark olive green	unchanged / changed / to blood red
Dandelion (yellow)	no effect	no effect
Phlox	olive green	red
Begonia	dark blue	red
Nasturtium	through olive green to brown	orange red
Petunia	greenish blue to green	purple red
Red rose	greenish blue to green	red
White rose	yellow	white
Cut leaf mallow	blue	red
Red poppy	purple	red
Field larkspur	green	red
Vetch	green	red
Bind weed { white / pink	yellow / green	white / pink
Portulaca { pink / crimson / blood red / yellow	lavender / purple / dark brown (almost black) / no effect	pink / crimson / blood red / no effect
Bachelor button (purple)	blue	red
Clover { white / red	yellow / green	white / red

It is noticeable that the yellows are not affected by acids or alkalies The whites are changed to yellow by alkalies and back to white again in acids

The reds and purples are changed to some shade of green or greenish blue by alkalies and usually back to the original color or a brighter red color by acids   These natural coloring substances seem to be quite generally acid in character, in some cases neutral

When it is observed that a certain flower or species of flower presents several different colors or shades of color, the question naturally arises, does each of these colors represent a different chemical compound?

Judging from the above observations, it seems likely that nature makes use of comparatively few basal coloring substances with which to produce many different colors by means of slight chemical changes. These substances are generally acid, sometimes neutral in character, and generally change color in acids and alkalies, alternately, acting as indicators. It is noticeable also that many of them are very sensitive to the action of light and air. The faintly colored alcoholic solutions of the Rose or the Perennial Pea, when evaporated to dryness, leave the bright red colored substance. The pink blossoms of the Perennial Pea, when picked and allowed to wilt, change to a violet color. The whole subject of natural coloring matters deserves a careful study from the chemical standpoint.

MANHATTAN, KANSAS.

THE PERIODIDES OF ACID AMIDES AND THEIR ADDITION PRODUCTS WITH METALLIC SALTS. SUBSTANCES OF EXCEPTIONALLY HIGH MOLECULAR WEIGHT.

BY F. J. MOORE AND RUTH M. THOMAS

It is well known that many organic bases form periodides usually containing more or less hydriodic acid, and that these substances, in their turn, form double compounds with metallic salts. The literature of such substances is extensive and widely scattered, and no complete review of it will be attempted here. It will be sufficient to call attention to the work of Geuther[1] who reviewed most of the work of others done up to this time; and that of François,[2] who devoted his attention chiefly to the periodides of the alkaloids. Little seems to have been done in the direction of preparing periodides of substances of the amide type, though Hoogewerff and van Dorp[3] studied the action of alkali and bromine upon the amide of benzene-m-disulfonic acid and observed the formation of a perbromide, $2C_6H_4(SO_2NBr_2)_2 + KBr + HBr$. Hofmann[4] noticed that acetamide formed a compound,

$$CH_3CONBr_2 + NaBr + H_2O.$$
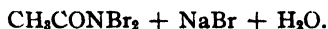
Titherley[5] observed the formation of double salts of acetamide such as $2CH_3CONH_2$, NaBr and $2CH_3.CONH_2$, NaI; and André[6] fused acetamide with various metallic salts and obtained different products, such as

$$2CH_3CONH_2.CoCl_2.H_2O;$$
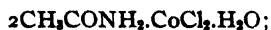
and Wheeler[7] also prepared some colored perhalides of acid anilides of

[1] Ann., 240, 66 (1887).

[2] J. pharm. et chim., [6] 30, 193 (1909).

[3] Rec. trav. chim., 8, 173 (1889).

[4] Ber., 15, 415 (1882).

[5] J. Chem. Soc., 79, 413 (1901).

[6] Jahresb. Chem., 1886, p. 1303; Compt. rend., 102, 115 (1886).

[7] Am. Chem. J., 18, 85 (1896); 19, 672 (1897).

the general type An.HI.I₂ and An₂.HI.I₄. Periodides of succinimide and its phenyl derivatives have also been prepared by Piutti.[1] These compounds had the general formula S₄ KI 3I and S₂ KI 2I. Finally there remain to be mentioned some derivatives of benzamide prepared by Curtius,[2] which will be discussed further on.

With the exception of the compounds mentioned by Curtius, Piutti, and Wheeler, substances of the properties described in the present paper seem not to have been prepared, which is rather remarkable in view of the ease with which they are formed and their rather striking physical properties Their preparation in this laboratory was in a certain sense accidental   In the course of an investigation upon the behavior of benzbromoamide, which has been going on here for several years, it seemed desirable for purposes of comparison to prepare benziodoamide   The method chosen was analogous to that hitherto in use for the preparation of the bromine compound [3]

Iodine was dissolved in cold alkali and benzamide was dissolved in the freshly prepared solution On acidification with dilute acetic acid, there was precipitated, not the colorless iodoamide which had been expected, but a dark green compound which preceded the precipitation of free iodine. It was found on experimentation that this substance could be best purified by solution in ether and subsequent dilution of this solution with benzene   In this way the material was obtained in long, green, hairlike needles of coppery luster   Later on, it was found that the use of alkali in the preparation was not necessary, and that, inasmuch as the product consisted only of benzamide, alkali iodide, and free iodine, the compounds could be readily prepared by heating together these ingredients in water.

Substances of this type were prepared in considerable number and showed many properties in common. They were for the most part immediately decolorized when shaken with metals such as silver or mercury, or upon the addition of alkali or sodium thiosulfate. The products formed were the amide and metallic salts

The simplest compounds were obtained either as addition products of amide, sodium or potassium iodide, and iodine, or else of amide, hydriodic acid and iodine, and the analysis showed that a few simple types, such as $(C_6H_5CONH_2)_2HI I_2$, $(C_6H_5CONH_2)_4NaI.I_2$, and $(C_6H_5CONH_2)_3KI.I_2$ were formed.

Solutions of the above compounds were treated with solutions of inorganic salts of other metals, in the expectation that the less soluble derivatives of the latter might be precipitated by metathesis. This was

[1] *Gazz chim ital* , **25**, II, 524 (1895)

[2] *Ber* , **23**, 3040 (1890)

[3] Moore and Cederholm, THIS JOURNAL, **28**, 1190 (1906)

not the case, but analogous compounds of barium and copper, for example, could be formed by warming the corresponding iodide with benzamide and iodine in water.

Substances of still a different type were formed when iodides of lead or mercury were warmed with benzamide, iodine, and potassium iodide. In these cases a product crystallized out which exactly resembled in appearance the simple potassium compound, but which also contained the heavy metal. This could not be removed by recrystallization, and analysis leaves little reason to doubt that the substances concerned are really "double" or "complex" salts, of the composition

$$((C_6H_5CONH_2)_3KI.I_2)_6PbI_2$$

and

$$((C_6H_5CONH_2)_3KI.I_2)_6HgI_2.$$
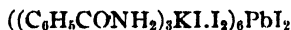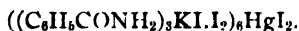
From similar indications, it was at first thought that analogous compounds, in which hydriodic acid replaced the potassium iodide, might be capable of existence. Since these products, however, on further purification showed a constant decrease in amount of heavy metal present, it is evident that such compounds, if they exist, are hardly stable enough for analysis.

The striking thing about the compounds mentioned is their high molecular weight. It will be seen that, for the lead compound, this reaches the value 5160, while the mercuric salt has a molecular weight of not less than 5152. In a series of synthetic experiments on the tannin group Emil Fischer[1] has recently prepared a complex derivative of maltose, which has a molecular weight of 4021, and which he describes as the compound having the highest molecular weight of any hitherto prepared by organic synthesis. The compounds here described are not, of course, "products of synthesis" in the same sense as those described by Fischer, all of which have been built up step by step, and to which there can be assigned definite constitutional formulae. They are, on the other hand, loose addition products of the "complex" variety, and are more or less dissociated in solution. Most of them, indeed, lose iodine in solution or in vacuum, and some frequently lose hydriodic acid; and it is doubtless a fact that their various components are held together by subordinate valences, in a sense analogous to the compounds which have been so extensively studied by Werner. Nevertheless, it is interesting that chemical complexes of such magnitude of any kind should be capable of isolation and stable enough to be recrystallized and analyzed.

The reactions above indicated yield analogous products with some other amides, both simple and substituted, but in the case of the simple amides the reaction does not seem to be as general as was at first supposed.

[1] *Ber.*, **46**, 3288 (1913).

Most of the anilides prepared, however, show the reaction well. The capacity of forming these compounds seems to be exceptionally highly developed in the case of benzamide, and it is here that it has received most study. Many tests, however, have been made with a variety of compounds, but it has not proved practicable up to the present time to lay down any rule which might connect the capacity for the formation of these periodides with the constitution of the amide employed. It is possible that some such regularity may be developed later.

Analysis.—When these compounds were to be analyzed the substances determined were usually total iodine, active iodine, and the metal, when present. Total iodine was almost universally determined by the Carius method, except when the presence of some other component suggested a difficulty. Active iodine was usually determined by adding water and benzene to the sample and then titrating with sodium thiosulfate until the pink color of iodine disappeared from the benzene layer. Here it was found that the addition of potassium iodide in considerable excess at the outset made it possible to titrate more rapidly, but did not change the numerical result, except in one or two cases, which are not even yet clearly understood. They will be mentioned in the experimental part. Metals were usually determined by the methods customary in such cases. When the methods of determination call for special consideration, they will be discussed under the individual compounds.

Experimental Part.

Periodides of Benzamide.

Benzamide, Sodium Iodide, and Iodine.--As indicated above, this substance was first prepared by dissolving iodine in sodium hydroxide, adding finely ground benzamide and acidifying with acetic acid in ice cold solution. It was soon found, however, that warming was advantageous, as it brought more iodine and benzamide into solution, and no decomposition was to be feared. A typical preparation is the following: 1.5 g. of benzamide were warmed with 10 cc. of 10% sodium hydroxide solution and 3 g. of iodine. On precipitation with dilute acetic acid 2 6 g. of crude product separated. This was purified by solution in ether and careful dilution with benzene, whereupon the product crystallized in long coppery green hairs. Yield, 2.15 g. The second crystallization yielded 1.30 g. of good product. The product was dried over sulfuric acid and had no odor of iodine when analyzed.

Calc. for $(C_6H_5CONH_2)_2NaI.I_2$: Na = 3.00%; active I = 33.11; total I_2 = 49 67. Found: 2 92, 3.05, 2.75, 3.12; 32.25, 31 85, 33.73; and 48.91, 48.77.

There seems to be little doubt but that this substance was once in the hands of Curtius. He prepared it by suspending the sodium salt of

benzamide in chloroform and adding iodine. He apparently overlooked the sodium content, and he arbitrarily assigned the formula

$$C_6H_5CO.NH_2.I$$
$$|$$
$$C_6H_5CO.NH_2.I$$

to the product, stating that he was unable to get concordant results on analysis. In order to test this assumption we prepared the same compound by treating sodium benzamide with iodine in ether. The product had the same appearance as the substance previously obtained and a sodium determination gave 2.44% sodium. Curtius had already observed that the product lost iodine when it was shaken with metallic mercury. We verified this fact, and found that molecular silver produced the same result. It was also decolorized by the action of aniline. When treated with trimethylphenylammonium iodide, the periodide,

$$(CH_3)_3C_6H_5.NI.I_2$$

was formed and benzamide could be isolated. All these reactions show an easy removal of the iodine from the rest of the molecule, indicating that it is held simply as in a loose addition product. It will be seen later that these periodides show varying degrees of stability in this respect. Sodium thiosulfate also removes the iodine rapidly, and this reaction was made use of in the determination of active iodine in these compounds.

Benzamide, Potassium Iodide and Iodine.—Most of the product was obtained by a method analogous to that first described for the sodium compound, but later it was observed that it was necessary only to warm the three substances together in water until they became entirely liquid. In one preparation 3 g. of benzamide were warmed with 1 g. of potassium iodide and 2 4 g. of iodine in 25 cc. water. On cooling, a pulpy . mass of greenish crystals filled the liquid. These were collected on a filter, dried, washed with carbon tetrachloride to remove any excess of iodine, and finally purified by solution in ether and crystallization by the careful addition of benzene. The product consisted of fine green hairs, which melted at $128°-130°$.

Calc. for $(C_6H_5CONH_2)_2KI.I_2$: $K = 4.98$, active $I = 32.44$; total $I = 48.66$. Found: 5.57, 5.61, 5 50, 30.01, 29 90, 30.74, 30.80; and 49 97, 49.60.

These results speak for a slight loss of active iodine during drying. No other rational formula corresponded quite so well with the results of the analysis.

It was found that the formation of the periodides was not limited to aqueous solvents. Thus 2 g. of benzamide, 1 3 g. of potassium iodide, and 3.1 g. of iodine, when warmed together in 10 cc. nitrobenzene, yielded 3.9 g. of an addition product which was apparently identical with that described.

Benzamide, Potassium Bromide and Bromine —Two grams of bromine were added to a mixture of 1 g of potassium bromide, 4 g of benzamide, and 15 cc of water The solid benzamide was instantly coated with a reddish substance When warmed on the steam bath the solid dissolved Rapid cooling resulted in the separation of beautiful green crystals which filled the tube When dried these crystals were brick red with a purple luster, but in the air they lost bromine too rapidly to permit of analysis

Benzamide, Potassium Bromide and Iodine —These substances, when heated together, gave a product which formed gray greenish hairs like the iodide derivative, with some unchanged benzamide Carbon tetra chloride removed scarcely any iodine The compound was not analyzed, but was evidently a double compound of the type suggested

Dibenzamide, Potassium Iodide and Iodine —These substances reacted smoothly when warmed with water on the steam bath The product was a green solid which appeared to be like the benzamide compound It was probably the potassium compound analogous to the one described by Curtius (*Loc cit*) and which probably contained sodium, although he overlooked that fact in his analysis, as already suggested The substance was not analyzed

Tribenzamide could not be made to react with iodine, either in the presence of potassium iodide or hydriodic acid

Benzamide, Hydriodic Acid and Iodine —Five grams of benzamide were treated with 10 cc of aqueous hydriodic acid (sp gr 1 90), which was already black with iodine 5 cc of water and 1 g of iodine were also added On warming, a black oil was formed which solidified when the solution cooled Washing with carbon tetrachloride removed some iodine, but left a crystalline product, which was dissolved in ether, and precipitated by carbon tetrachloride in tiny flakes, showing a green-black iridescence Yield of purified product, 8 5 g

Calc for $(C_6H_5CONH_2)_2HI\ I_2$ Active I = 40 70, total I = 61 05 Found 37 92, 38 88, 38 93, and 61 45 61 32

It is interesting to note that the color of this compound differs from that of the corresponding sodium and potassium compounds, and also that this substance contains two benzamides instead of three, as in previous cases

Benzamide, Barium Iodide and Iodine —The best proportions were 1 molecule of benzamide, 6 molecules of barium iodide and 4 atoms of iodine These were warmed together in the presence of water The solid product when treated with ether formed a black oil, and this, when treated with benzene, yielded a precipitate consisting of chocolate brown flakes and needles which were steely blue by reflected light The sub stance belongs to the less stable members of this class and dissociates somewhat in solution On crystallizing it, if too much free iodine is

present in the solution, the product comes out oily, and, on the other hand, the presence of too little iodine results in the separation of barium iodide. Crystallization from pure solvent causes loss of iodine, so that in this, as well as in several other cases, it is advisable to add iodine judiciously to the solvent.

Barium was determined directly by smoking off with sulfuric acid and also, as a check, by precipitation from the filtrates from the silver iodide in the Carius determination of total iodine.

Calc. for $(C_6H_5CONH_3)_2BaI_3.I_4$: Ba = 8.43; active I = 31.26; total I = 46.89. Found: 8.49, 8.53, 8.52; 31.20, 31.49; and 44.96, 44.80.

It should be added that numerous other determinations of active iodine from different samples gave results as much as 2% lower than those here quoted. The tendency to dissociation above mentioned seems to account for this.

Benzamide, Cuprous Iodide and Iodine.—1.5 g. of slightly moist cuprous iodide, 1.5 g. of benzamide, and 3 g. of iodine were warmed with water on a steam bath. The iodine melted to a lower layer, and most of the solid dissolved. The aqueous layer was filtered hot. In the filtrate coppery needles were formed, while upon the surface of the liquid there appeared a fine film of cuprous iodide. This could be removed mechanically. The copper-colored needles were collected by filtration. They were sometimes mixed with benzamide, from which they could be separated mechanically. They melted at about 90° to a black liquid. This substance lost weight very rapidly when an attempt was made to dry over phosphorus pentoxide, and over alkali the loss was also rapid, so that a sample which had stood six weeks contained only 4.5% active iodine. The material used for analysis was therefore dried rapidly in the air. Numerous determinations were made, and particular pains taken with the analysis, but the results were not very satisfactory. Difficulty was experienced in the determination of active iodine, in that the end point of the titration was changed by the addition of potassium iodide. No thoroughly adequate explanation has been found for this. Copper was determined first by smoking off directly with nitric acid and weighing as oxide; second, according to Bray,[1] by conversion to sulfate, and titration against sodium thiosulfate after addition of potassium iodide; and third, by Jörgensen's[2] method, of treatment with sulfurous acid and weighing as cuprous iodide. The iodine in the filtrate from the cuprous iodide was precipitated with silver nitrate.

On account of the beautiful appearance of this compound numerous analyses were made. As stated above, the results were not entirely satisfactory, those quoted being some of the best.

[1] THIS JOURNAL, **32**, 1208 (1910).

[2] *J. prakt. Chem.*, [2] **2**, 353 (1870).

Calc for $(C_6H_5CONH_2)_2CuI I_6$ Cu = 3 31, Cu_2I_2 = 9 32, active I = 39 66, total I = 46 26   Found 3 27 3 13 3 16, 3 81, 3 47, 3 43, 10 28, 9 75, 10 28, 37 99, 36 18, 36 80, 37 10, and 45 43, 46 01, 47 55 47 30

It may be stated, in general, that the determinations for active iodine which differed most widely varied between 35 66 and 40 06

Benzamide, Cobalt Iodide and Iodine —Two grams of cobalt iodide were warmed with 1 6 g of benzamide, 2 6 g of iodine and 10 cc of water on the steam bath On cooling, a green precipitate settled out, which could be purified by dissolving in ether and precipitating with carbon tetrachloride It was not analyzed

Nickel iodide also yields a similar product Attempts to prepare corresponding compounds, using silver iodide, lead iodide, mercuric and mercurous iodide, all resulted without success

Benzamide, Potassium Iodide, Mercuric Iodide and Iodine Ten grams each of benzamide and iodine were warmed with 100 cc of 10% potassium iodide solution, to which mercuric chloride had been added until mercuric iodide began to precipitate The resulting crude product weighed 23 g. The filtrate contained little free iodine The precipitate was dissolved in 150 cc of ether containing 5 g of iodine A dirty gray residue of benzamide was removed which weighed about 2 g The filtrate was then treated with 250 cc of benzene and later, as precipitation took place slowly, with 100 cc more The solution at this point was purple and very full of crystals The solution was filtered by suction and the crystals were washed with benzene Four crops in all were obtained, of which about 9 g made up the first, which was very pure Repeated crystallization of the entire product made little or no difference in the mercury content A sample for analysis was dried over caustic alkali, and melted in the air at about $50°$ Mercury was determined as sulfide, following the method described in Treadwell's 'Analytical Chemistry "[1]

Calc for (1) $((C_6H_5CONH_2)_2KI I_2)_7HgI_2$, (2) $((C_6H_5CONH_2)_2KI I_2)_6HgI_2$ (1) K = 4 62, Hg = 3 37, active I = 29 06 total I = 49 20, (2) K = 4 56, Hg = 3 88, active I = 29 57, total I = 49 30   Found 4 49, 4 48, 3 34 3 30 3 56, 30 36, 30 42, and 48 52, 48 42

The analysis hardly gives sufficient data to decide between the two formulas quoted

Benzamide, Potassium Iodide, Lead Iodide and Iodine —One and five tenths grams of lead iodide and 5 g of potassium iodide mixed in 15 cc. water gave a fine pale yellow precipitate of a double compound To this were added 10 g each of benzamide and iodine The product melted entirely on the steam bath and solidified on cooling It was dried as thoroughly as possible, the process being difficult on account of the lumping of the material The product was dissolved in ether containing considerable iodine and crystallized on addition of benzene in gray-green

[1] (Hall) 3rd Ed, Vol II, 169

hairs. The first crop of 6 g. gave a strong test for lead; the later crops, not so strong. When the first crops were recrystallized, however, a perceptible decrease in lead content was not noted. In analyzing the product, lead and potassium were changed together to sulfate by smoking off with sulfuric acid and subsequent ignition. The precipitate was then digested thoroughly with dilute sulfuric acid (1 : 20), cooled completely, filtered and washed with 1 : 20 acid, followed by 1 : 1 alcohol, the precipitate being weighed as lead sulfate. The solution was evaporated and the residue ignited and weighed as potassium sulfate. The iodine here was not determined by the Carius method as it was feared that the silver iodide formed might be contaminated with lead iodide, and instead the sample was digested with sodium carbonate solution, filtered, and washed. The filtrate was treated with sulfurous acid to reduce any iodate to iodide, and finally precipitated with silver nitrate.

Calc. for $((C_4H_5CONH_2)_3KI.I_2)_6PbI_2$· K = 4.55; Pb = 4.01, active I = 29 54; total I = 49.22. Found: 4.30; 3.96; 30.14; and 49.26

The above results were obtained from one recrystallized sample, representing the purest product available.

Benzamide, Mercuric Iodide, Hydriodic Acid and Iodine.—An attempt was made to prepare a compound which combined all the above four components, and as a matter of fact crystals were obtained. These, however, did not prove sufficiently stable to permit of analysis, and in the course of crystallization the mercury content steadily decreased.

Experiments with Other Amides and with Anilides.

p-Toluamide, Potassium Iodide and Iodine.—Five-tenths gram of p-toluamide (2 mols), o 3 g. of potassium iodide (1 mol), and o.5 g. of iodine (2 at.) were rubbed together with 2 cc. of water. They formed a thick pulp in a few minutes. The yield was 1 2 g. The color was not removed by carbon tetrachloride. The product was purified by adding carbon tetrachloride to the ethereal solution, and it too formed coppery green hairs. The analytical results on the different samples were not concordant and it is probable that the small quantity prepared did not permit of adequate purification. The substance contained about 5% of potassium. p-Toluamide, when warmed with hydriodic acid and iodine, gave a fine grayish black crystalline precipitate, which was practically insoluble in boiling carbon tetrachloride. This has not yet been analyzed. o-Toluamide gave no addition product with potassium iodide and iodine. With hydriodic acid and iodine it gave a black tar which would not crystallize.

p-Bromobenzamide gave a greenish precipitate with potassium iodide and iodine. m-Bromobenzamide, on the other hand, did not react.

The three nitrobenzamides were next tested, and in this case the m- and p-compounds gave crystalline products, but the o-compound did not.

Experiments were then made with several other amides, including some belonging to the aliphatic series. No addition products were obtained with acetamide, salicylamide, oxamide, or succcinamide. Succinimide, on the other hand, gave, with potassium iodide and iodine, the addition product $(C_4H_5O_2N)_4.KI.I_3$. This substance had already been prepared and described by Piutti (*Loc. cit*). Phthalimide also gave an addition product with potassium iodide and iodine which has not yet been analyzed. Benzene sulfonamide gave a fine greenish brown precipitate. Experiments with urea, thiourea and benzoylphenylurea all gave negative results.

Anilides.—Attention was next turned to the anilides, and here it was found that the reaction was fairly general, although substances which gave addition products with potassium iodide and iodine frequently did not do so with hydriodic acid, whereas in certain other cases this relationship was reversed. Among the compounds tested are acetanilide, benzanilide, phenylacetanilide, diphenylbenzanilide, aceto-*o*-toluidide, aceto-*p*-toluidide, benz-*o*-toluidide, and methylacetanilide. In the case of a few of the products formed, analyses have already been made, but it seems best to postpone the discussion of these addition products until some more work has been done. They will, accordingly, be reserved for some subsequent paper.

Summary.

1. Benzamide and some other amides form complex periodides containing iodine and hydriodic acid, or else some metallic iodide. The general composition of most of these compounds is $Am_3.MeI.I_2$ and $Am_2.HI.I_2$, though other combinations are observed.

2. Similar reactions seem to be very general in case of substituted anilides.

3. The compounds described in (1) can exist in combination with iodides of heavy metals, like lead and mercury, forming complex molecular aggregates of exceptionally high molecular weight.

MASS. INST. TECHNOLOGY, BOSTON, MASS

STUDIES IN BACTERIAL METABOLISM.

BY ARTHUR I KENDALL, ALEXANDER A DAY AND ARTHUR W WALKER

XXXI. The Metabolism of the Typhoid-Dysentery-Alcaligenes Group in Milk.

One of the great problems in modern civilization is that of safeguarding that great river of milk which flows daily into practically every city and town. This problem in the last analysis is a bacterial problem, for those

changes which render milk unfit for food are induced in it by the growth of microörganisms. Time, temperature, and the kinds of bacteria which find their way into milk largely determine the changes which it undergoes before it is finally consumed or ultimately unfitted for food. When milk is abnormal to sight and taste, it is no longer salable, but unfortunately these somewhat crude indicators are of little service in detecting the presence of microörganisms which may be more dangerous to health or even life than those which produce the more marked decompositions.

Except in a qualitative way, little is definitely known of the nature or even extent of bacterial action on milk. Souring (coagulation), peptonization, ropiness, and slimy milk are well-known chemical changes which may be regarded as decompositions readily recognizable by the layman as well as by the specialist; but the absence of such obvious changes in physical appearance cannot, in any sense, be a criterion for judging of the fitness of milk or of the products made from it for human consumption. That is to say, the esthetic appearance is not necessarily synonymous with safety —indeed, it may be absolutely the reverse. It should be remembered that milk is much more complex in composition than the ordinary media generally used for bacterial cultivation. This complex fluid, which is a well balanced food for man, contains fats, protein, carbohydrates and salts, the latter probably partly free and partly combined with the protein, all dissolved or suspended in water. With such a variety of constituents to act upon, the decompositions which it undergoes will vary greatly, with the type of organism or organisms which gain access to it and the conditions under which the milk is kept.

Certain types of decomposition might be confidently predicted. Those organisms which attack lactose vigorously would produce greater or lesser amounts of acid by the fermentation of this sugar, with but little coincident action upon the protein, for previous experiments have shown that fermentation takes precedence over putrefaction.[1] With respect to the protein sparing action of fats but little can be stated definitely at the present time. Fats, however, would appear to have but little influence upon the protein sparing action of utilizable carbohydrate, for experiments would suggest that fats are less readily utilizable by the ordinary lactose-fermenting bacteria than are carbohydrates.

Any milk which is available for cultural purposes has undergone a certain amount of decomposition, for bacteria in greater or less numbers are always found in it; indeed, there is strong evidence that even milk drawn from the cow with sterile precautions practically always contains some bacteria.[2] The effect of this early bacterial development upon the

[1] Kendall, *J. Med. Research*, **25**, 155 (1911)

[2] Harding and Wilson, *Tech Bull.* **27**, N Y Agr Exp Station, Mar, 1913. For résumé of literature

composition of the milk prior to sterilization for cultural purposes cannot be predicted   The situation is further complicated by the effect of symbiotic growth of bacteria, for it has been shown, for example,[1] that $B\ coli$ and $B\ mesentericus$, growing symbiotically in milk, produce changes as the result of their mutual development which are greater in intensity and different in kind than the sum of their separate activities   Nevertheless, the best obtainable grades of market milk do not as a rule, show demonstrable deviations in composition from freshly drawn milk   The observations recorded below were made for the purpose of determining the nature and extent of the changes brought about by the growth of various important types of bacteria in sterile certified milk   These determinations include the changes in reaction, as shown by alizarin, neutral red, and phenolphthalein, which indicate somewhat roughly the differential accumulation of alkaline or acid products, and the action on protein as represented by the accumulation of ammonia, ammonia being the only available index of protein breakdown applicable to this problem   The exact analytical details have been published elsewhere [2]   The cultures have been incubated uniformly at body temperatures   Growth is more rapid under these conditions with the organisms used, and the accumulation of metabolic products should be proportionately greater for this reason, particularly during the early days of incubation   These conditions are not met with in the practical handling of milk but are resorted to here in order to exaggerate the changes which probably would take place at a lower temperature with the same organisms in the same time   Furthermore, it is obvious that pure cultures of bacteria would never be met with in practice, although the net results of associated activity of bacteria in milk are in the last analysis the ones which are of practical importance   An initial investigation, in which the activity of each particular type of organism, *per se*, is studied, should serve as a fundamental introduction to the much more complex subject of bacterial antagonism and symbiosis as it presents itself in the milk problem

   Certain analytical difficulties might be anticipated, particularly in the case of those organisms which cause coagulation, peptonization, or other rather marked physical changes in milk, because of the difficulty in obtaining uniform samples for analysis   While these difficulties have been realized to a certain degree, the determinations which have been made in duplicate have not shown noticeable variations, except in those instances where analyses of the residual milk fats were attempted   The difficulties of obtaining uniform samples for these determinations have been found to be so great that observations along this line have been temporarily discontinued   They will be resumed at a later date, using the modifica-

[1] Kendall, *Boston Med and Surg J*, 163, 322 (1910)
[2] Kendall and Farmer *J Biol Chem* 12, 13 (1912)

tions of the methods stated above, namely, by introducing the appropriate amounts of milk containing cream into Babcock bottles, sterilizing, inoculating, and making the determinations on the entire sample removed at the appropriate time. The results are given in Table I.

TABLE I

Days	Whole milk					Whole milk				
	Alizarin	Neutral red	Phenolphthalein	NH₃ mg increase per 100 cc milk	NH₃ total N₂ per cent	Alizarin	Neutral red	Phenolphthalein	NH₃ mg increase per 100 cc milk	NH₃ total N₂ per cent
	B alcaligenes					*B dysenteriae*, Flexner.				
1	—0 10	+0 20	—0 10	—0 70	—0 11	+0 30	+0 80	+0 70	0 00	0 00
3	—0 20	—0 30	—0 60	—0 70	—0 11	+0 40	+0 40	+0 20	0 70	0 11
7	—0 90	—1 60	—0 80	+5 60	0 92	+0 30	+0 20	—0 10	0 70	0 11
14	—1 60	—1 90	—2 00	+4 20	0 69	—0 10	0 00	—0 30	0 70	0 11
21	—1 40	—2 00	—2 10	+5 60	0 92	—0 40	—0 10	—0 40	1 40	0 23
28						—0 40	—0 20	—0 60	1 40	0 23
	B dysenteriae, Shiga					*B typhosus*				
1	+0 50	+1 00	+1 00	0 00	0 00	+0 30	+0 70	+0 70	—0 70	—0 11
3	+0 10	+0 70	+0 70	0 00	0 00	+0 10	+0 80	+2 90	0 00	0 00
7	+0 40	+0 80	+0 50	0 70	0 11	0 00	+0 70	+2 90	1 40	0 23
14	—0 40	+0 40	+0 10	0 70	0 11	+0 20	+0 30	+2 90	5 60	0 92
21	—0 20	—0 10	—0 20	1 40	0 23	+0 10	+0 50	+1 90	6 30	1 15
28	—0 20	—0 20	—0 40	2 80	0 46	+0 60	+0 50	+1 60	5 60	0 92

B. alcaligenes, an organism which ferments no sugars, produces a slightly alkaline reaction in milk, coincident with a slight increase in the ammonia content, amounting to rather less than 1% of the total nitrogen. These results are in harmony with what is known qualitatively of the changes produced in milk by this organism, and the intensity of the reactions corresponds closely with that obtained under similar conditions in broth cultures [1]

The Flexner and Shiga types of the dysentery bacillus exhibit an initial acidity followed by a definite return to alkalinity, the degree of alkalinity being greater than that of the inoculated milk. There is very little action upon the protein constituents of the milk. The explanation of this initial acidity followed by an alkaline reaction was first clearly demonstrated by Theobald Smith, who showed by presumptive evidence that market milk normally contains a substance which bacteria utilize like dextrose, the amount being about 0 1%. It will be remembered that the dysentery bacilli and *B. typhosus*[2] utilize dextrose in preference to protein for fuel purposes, consequently this initial acidity observed in milk cultures

[1] Kendall, Day and Walker, THIS JOURNAL, **35**, 1216 (1913)

[2] Kendall, *J Med Research*, **25**, 155 (1911)

is due to the fermentation of this dextrose-like substance which Theobald
Smith has described.[1] The organisms do not ferment lactose, and the re-
turn to alkalinity is doubtless due to the formation of basic products from
protein which the dysentery bacilli are forced to utilize when this dex-
trose-like substance is exhausted. It will be noticed that the typhoid
bacillus does not exhibit a return to the alkaline reaction. It produces,
however, a certain amount of ammonia, indicative of protein breakdown,
which appears to be somewhat greater in amount than that produced by
the dysentery bacilli and comparable to the amount produced by *B.
alcaligenes*. The extent of this protein breakdown, however, is very little,
amounting to but 6 3 mg. in 100 cc. of milk in three weeks.

The question might be raised whether this dextrose-like substance
which is fermented by the dysentery and typhoid bacilli is not in reality
a mixture of dextrose and galactose formed by the hydrolytic cleavage
of lactose during the process of sterilization. A series of experiments con-
ducted in this laboratory, which will be published later, have fully cor-
roborated the observations of Theobald Smith, mentioned above, that
such is not the case. The substance which reacts like dextrose is a normal
constituent of milk. Further evidence of the correctness of the assump-
tion that fermentation of this dextrose-like substance in milk is responsi-
ble for the initial acid reaction produced by the dysentery and typhoid
bacilli is furnished by the results obtained in milk to which 1% of dex-
trose has been added. These organisms produce enough acid in this dex-
trose milk to cause its coagulation.

This explanation, furthermore, furnishes additional proof of the correct-
ness of the assumption that the terminal alkaline reaction exhibited by
the dysentery bacilli is due, in part at least, to the breakdown of protein
constituents of milk following the exhaustion of the dextrose. The addi-
tion of 1% of dextrose protects this milk protein from attack and the re-
action becomes in the latter case progressively acid.

The persistance of an acid reaction in milk cultures of typhoid bacilli
is not so readily explained. An explanation of this reaction on the basis
of the fermentation of lactose is wholly out of the question, for the typhoid
bacillus does not, under any conditions, utilize this sugar. It is conceiv-
able that this organism in breaking down protein after the exhaustion of
the dextrose acts upon casein in such a manner as to liberate phosphoric
acid, perhaps in the form of acid phosphates. Another possible explana-
tion is the formation of slight amounts of fatty acids from certain constit-
uents of the milk fat.

Conclusions.

1. *B. alcaligenes*, the Flexner and Shiga types of the dysentery bacillus,
and *B. typhosus* produce no marked alterations in the appearance of milk,

[1] Smith, Theobald, *J Boston Soc Med. Sci.*, **2**, 236 (1898)

nor any noteworthy changes in the composition of milk as indicated by the gross appearance, the changes in reaction, and ammonia production.

2. The presence even of large numbers of these organisms in market milk could not be detected by chemical methods available at the present time during the period when this milk would be salable.

3. The production of an initial acidity followed by an alkaline reaction, which is a well-known cultural characteristic of the dysentery bacilli, is explainable on the basis of the chemical changes which these organisms produce in this medium.

4. The explanation of the permanent acidity exhibited by cultures of typhoid bacilli in milk is not definitely determined.

XXXII. The Metabolism of the Intermediate or Paratyphoid Group in Milk.

The cultural reactions in milk of bacteria belonging to the intermediate or paratyphoid group are, generally speaking, qualitatively like those of dysentery and typhoid bacilli; namely, in the case of *B. paratyphosus alpha* a permanent acid reaction, while other members of this group exhibit an initial acidity followed by a return to alkalinity, resembling the members of the dysentery group in this respect. These observations apply only to the earlier days of growth, however, for it is a matter of common observation that older milk cultures of the paratyphoid group change somewhat in appearance. Cultures of *B. paratyphosus alpha* tend to become somewhat less acid than cultures of the typhoid bacillus, while cultures of *B. paratyphosus beta* and the remaining members of the group become almost opalescent as time goes on, due apparently to a gradual solution of the casein.

The chemical changes which these organisms produce in milk, shown in Table II, resemble those of the dysentery bacilli in a striking manner, both qualitatively and quantitatively, except for the gradual thinning of the medium, mentioned above. This latter phenomenon does not appear to be associated with a noteworthy increase in the amount of ammonia formed or to an unusual degree of alkali production. *B. paratyphosus alpha* produces changes in milk which, measured in terms of changes in reaction and production of ammonia, are very similar to those exhibited by the typhoid bacillus, except that the degree of acidity reached appears to be rather less. This acidity is permanent and is one of the most important cultural characteristics of this organism. This permanent acidity is a noteworthy characteristic of milk cultures of both these organisms. Whether the explanation of this acidity is the same in both cases cannot be stated definitely. *B. paratyphosus beta* differs chemically from *B. paratyphosus alpha* in that the period of initial acidity is followed by a progressively alkaline reaction, the final degree of alkalinity being noticeably greater than that of the uninoculated control. The amount of ammonia

TABLE II.

Days	Whole milk.					Whole milk.				
	Alizarin	Neutral red	Phenolphthalein	NH₃ mg. increase per 100 cc milk	NH₃ total N, per cent.	Alizarin	Neutral red	Phenolphthalein	NH₃ mg. increase per 100 cc milk	NH₃ total N, per cent.
	B paratyphosus alpha					*B icteroides*				
1	+0 30	+0 60	+0 70	—1 40	—0 23	+0 40	+0 50	+0 60	2 10	0 34
3	+0 60	+0 80	+0 90	0 70	0 11	—0 70	—0 60	—0 90	1 40	0 23
7	+0 50	+0 70	+1 00	1 40	0 23	—0 40	—1 60	—1 90	2 80	0 46[4]
14	+0 90	+1 10	+1 70	1 40	0 23	—0 20	—3 50	—2 20	2 10	0 34[5]
21	+1 10	+1 00	+0 70	4 20	0 69	—0 40	—3 80	—2 30	2 80	0 46[6]
28	+0 60	+0 60	+0 50	4 20	0 69	—0 40	—3 60	—2 40	3 50	0 57
	B paratyphosus beta					*B Morgan No 1*				
1	+0 30	+0 50	+0 60	—0 70	—0 11	—0 10	0 00	+0 50	2 10	0 34
3	—0 70	—0 10	+0 70	0 00	0 00	—0 90	—0 30	+0 40	1 40	0 23
7	—0 60	—1 40	+1 40	1 40	0 23[1]	—1 30	—0 20	+0 70	14 00	2 30
14	—0 80	—2 20	—1 90	2 10	0 34[2]	—0 80	—0 20	+0 80	14 00	2 30
21	—0 50	—1 90	—2 10	2 80	0 46[3]	0 00	+0 20	+1 00	12 60	1 98
28	—0 90	—2 40	—2 00	4 20	0 69					

[1] Milk thin
[2] Milk thin, somewhat brownish
[3] Milk very thin, brownish
[4] Milk somewhat thin
[5] Milk decidedly thin
[6] Milk very thin, brownish

produced is practically the same as that formed by *B. paratyphosus alpha* in milk.   By the end of the first week milk cultures of *B. paratyphosus beta* become slightly brown in color and distinctly thinner in consistency than normal milk, and after two or three weeks' incubation the milk becomes almost opalescent.

B. icteroides was at one time regarded as the etiological factor in yellow fever; it is now classified as a member of the hog cholera group.   Culturally it resembles *B. paratyphosus beta*, and this cultural resemblance is also manifested chemically, the reactions of the two organisms being very similar.   This same brownish decolorization and thinning of milk culture of *B. paratyphosus beta* is also a prominent feature of milk cultures of *B. icteroides*.

The Morgan bacillus, which it will be remembered is rather frequently met with in the dejecta of babies suffering from diarrhea,[1] is more proteolytic than the other members of the intermediate group.   This is in accord with similar observations made in broth cultures.[2]

Conclusions.

1. Milk containing *B. paratyphosus alpha*, *B. paratyphosus beta*, *icteroides*, or the Morgan bacillus, exhibits no noteworthy changes in che

[1] Morgan, *Brit Med J.*, Apr. 21, 1906, p. 908; July 6, 1907, p 16, Kendall, L.̂ and Bagg, *Boston Med and Surg. J.*, 169, 741 (1913).

[2] Kendall, Day and Walker, THIS JOURNAL, 35, 1221 (1913).

ical composition, particularly during the early days of incubation. The gradual decrease in opacity, which is a characteristic of old milk cultures of *B. paratyphosus beta* and *B. icteroides* will be of no practical value in detecting the presence of these organisms in market milk.

2. The initial acidity exhibited by all the members of the paratyphosus group is similar in origin to that of the typhoid-dysentery group, due to the fermentation of the dextrose-like substance which appears to be a normal constituent of fresh milk.

3. *B. paratyphosus alpha* reacts like *B. typhosus* in milk, that is, it produces a permanent acidity. The cause of this permanent acidity is not definitely known.

4. The Morgan bacillus is more proteolytic than the other members of the intermediate group.

XXXIII. The Metabolism of the Coli-Proteus-Cloacae Group in Milk.

Among the organisms commonly found in milk are *B. coli, B. proteus*, and, perhaps to a lesser extent, *B. cloacae*. *B. coli*, furthermore, is an organism found constantly in the intestinal tract of man and mammals, and its presence in milk is popularly supposed to indicate contamination with fecal matter, hence its presence is frequently regarded as an indication of filth. This conception is undoubtedly attributable in the last analysis to the importance of the colon bacillus as an indicator of pollution in water. The numbers of colon bacilli which may be present in a sample of milk do not necessarily furnish any evidence of the nature or extent of fecal contamination, for there is no way of distinguishing between the initial number of these organisms in a given sample of milk and their descendants. Furthermore, colon bacilli have been shown by many observers to occur in large numbers on dried grains and hay. These organisms are readily detached from these grains, and, together with dust, may readily find their way into the milk pail quite independently of any direct fecal contamination. The subsequent development of *B. coli* and the numbers of it which appear in milk are the results of time and temperature rather than initial seeding, for this organism grows very rapidly in this medium. The analyses recorded in the accompanying chart show that *B. coli* does not attack milk proteins to any appreciable extent, and this might have been confidently predicted, for *B. coli* acts energetically upon lactose, bringing about coagulation in from 24 to 72 hrs. as a rule   The resulting product is potentially buttermilk, that is to say, a pure culture of this organism produces a marked lactic acid fermentation with acid coagulation of the casein. The degree of acidity produced is quite considerable, amounting to more than 5% reckoned in terms of normal acid by the end of the third day. It is a noteworthy fact that *B. coli* does not produce noticeable amounts of gas in milk, although the lactose content of this medium is several times that of lactose broth, in which medium

a considerable amount of gas is formed. No satisfactory explanation of this phenomenon is available. It is worthy of note, however, that gas formation proceeds rapidly in milk when *B. coli* is grown symbiotically with certain actively peptonizing bacteria, notably strains of *B. mesentericus*.[1] Here gas formation is actually greater than is the case when *B. coli* is grown in pure culture in lactose broth.

TABLE III

Whole milk

Days	Alizarin	Neutral red	Phenolphthalein	NH_3 mg increase per 100 cc milk	NH_3 total N_2 per cent
			B coli		
1	+0 10	+1 70	+0 20	0 00	0 00
3	+0 50	+4 40	+5 50	0 00	0 00[1]
7	+1 90	+4 30	+5 60	1 40	0 23[1]
14	+2 50	+4 90	+5 30	1 40	0 23[1]
21	+2 90	+5 30	+6 20	2 10	0 34[1]
28	+3 20	+6 40	+6 00	1 40	0 23[1]
			B cloacae		
1	—0 10	+0 40	+0 80	2 10	0 34
3	+0 50	+0 70	+0 90	1 40	0 23
7	+0 50	+1 70	+1 20	3 50	0 55[2]
14	+2.50	+2 10	+3 80	4 20	0 69[2]
21	+2 70	+1 80	+3 00	5 60	0 92[2]

Whole milk

Days	Alizarin	Neutral red	Phenolphthalein	NH_3 mg increase per 100 cc milk	NH_3 total N_2 per cent
			B proteus.		
1	+0 30	+0 60	+0 60	8 40	1 35
3	+1˙60	+1 10	+2 80	16 80	2 70[3]
7	+1 90	+2 90	+4 80	27 30	4 38[4]
14	+0 80	+3 00	+5 10	32 20	5 17[5]
21	+1 10	+3 50	+5 30	37 10	5 96[5]
28	+3 20	+2 00	+5 70	36 05	5 85[5]
			B proteus (20°)		
1	—0 10	+0 30	+0 90	4 90	0 7[1]
3	+1 40	+0 70	+1 60	14 70	2 3[1]
7	+1 30	+1 90	+3 80	22 40	3 53[4]
14	+1 50	+3 60	+4 50	33 60	5 28[5]
21	+1 70	+3 40	+4 60	34 30	5 40[5]

[1] Coagulated   No gas
[2] Coagulated   Somewhat viscid, no gas
[3] Coagulated, peptonized
[4] Coagulated, marked peptonization
[5] Coagulated extensive peptonization

B. cloacae is probably far less commonly met with in milk than *B. coli* or *B. proteus*, although it is frequently found in sewage and sewage polluted water. This organism, like *B. coli*, ferments lactose, but it will be observed that the degree of acidity attained is scarcely one-half that produced by the colon bacillus under the same conditions. The same phenomenon is met with in lactose broth. The degree of proteolysis, as measured by the increased ammonia, is about twice that of the colon bacillus, reckoned in terms of milligrams of ammonia per 100 cc. of milk. The amount, however, is not great, being less than 6 mg. in 100 cc., or 60 parts in a million parts of milk. These chemical changes agree closely with those described for this organism in broth cultures[2] so far as the initial stages are concerned. *B. cloacae*, however, does not appear to form alkali in milk even after prolonged cultivation, although it forms alkali in sugar

[1] Kendall, *Boston Med. and Surg. J.*, 163, 322 (1910)
[2] Kendall, Day and Walker, THIS JOURNAL, 35, 1227, 1230 (1913)

TABLE IV.

Whole milk.

Days	Alizarin	Neutral red	Phenolphthalein	NH₃ mg. increase per 100 cc. milk	NH₃ total N, per cent.	Remarks.
						B. subtilis.
1	0.00	0.00	—0.10	0 00	0.00	
3	+0.20	—0.30	—0.40	7.70	1.23	Coagulated; slight peptonization
7	—0.30	—1.60	—0 30	23.8	3.76	} Marked peptonization
14	—1.50	—2.70	....	73.5	11.80	
21	....	—1.80	—1.40	92.5	14.80	} Coagulated; extensive peptonization
28	....	—3.30	—2 30	109 9	17.62	
						B. mesentericus
1	+1.00	+2.80	+3.20	4.20	0.67	
3	+1.90	+4 90	+6 20	11.90	1.91	Coagulated. Some peptonization.
7	+2.30	+5 20	+7 00	32 20	5.17	
14	....	....	+6.90	56.70	9.10	Coagulated. Extensive peptonization
21	+3.00	+2.50	+5.60	95.20	15.30	
28	+3.80	+4.20	+6.60	110.40	17.70	
						B. pyocyaneus.
1	+0.10	+0.20	+0.10	0.70	0.11	Cream ring slight green-blue.
3	+2.30	+0.70	+1.30	6.30	1.01	Medium thin, yellow-green; slightly viscid
7	+1.20	—1.40	—0.50	51.10	8.20	Medium thin, green-yellow, very viscid
14	+0.30	—2.00	—0.10	123.20	19.80	} Very thin, green, very viscid.
21	....	....	—0 20	171.10	27.50	
28	....	. ..	—1.90	159.90	25.65	

Bacteriologists are by no means in accord in defining precisely the characters which differentiate the members of the hay bacillus and potato bacillus groups. Theobald Smith states that *B. subtilis* ferments no sugars, that is, it is an obligate proteolyte, in other words, and his classification is accepted without question in this work. *B. mesentericus* ferments dextrose, and there is considerable evidence that it forms fatty acids, at least to a moderate extent, from milk fats. Both of these organisms have been found to break down the protein of milk energetically, as is shown in the accompanying tables. This breakdown, furthermore, continues without interruption for at least four weeks at the body temperature, so that there is produced at the end of this time 110 mg. of ammonia above that of the uninoculated controls kept under the same conditions. This breakdown of protein results in the liberation of ammonia which corresponds to nearly 18% of the total nitrogen of the milk. Even these active proteolytic organisms, however, do not produce any considerable amount of protein breakdown during the first 24 hrs. of growth at body

temperature, and it is almost certain that if they were kept at room temperature, that the temperature at which milk is ordinarily shipped, that is, below 7°, these changes would be scarcely detectable in the first few days. This should not be construed, however, to mean that milk containing considerable numbers of these organisms is a fit food for infants.

B. *subtilis* produces a progressively alkaline reaction in milk, which is readily explainable on the basis of the decomposition of the milk proteins, resulting in the accumulation of ammonia and other basic products. At the third day peptonization is well marked. This peptonization continues until the casein of the milk is almost completely liquefied. B. *mesentericus* produces a progressively acid reaction which manifests itself in spite of the very considerable decomposition of protein and accumulation of ammonia, resembling B. *protens* in this respect.[1] The initial acidity is attributable to the fermentation of the small amount of dextrose or dextrose-like substances normally present in milk. The subsequent development of acid is perhaps due, in part at least, to the breakdown of milk fat and the liberation of fatty acids. Whether a coincident liberation of acid phosphates takes place cannot be stated.

B. *pyocyaneus* is rarely found in milk which has been properly handled, but it may occasionally find its way into milk through contaminated water, for this organism is sometimes found under these conditions. It is even more active proteolytically than either B. *subtilis* or B. *mesentericus*, and at the end of the third week more than 170 mg. of ammonia, amounting to 27.5% of the total nitrogen in milk, has accumulated. During the first 24 hrs. of incubation the milk becomes blue-green in color, particularly the cream layer, and by the end of the third day the milk is decidedly green throughout. It is then very viscid. By the end of the second week the milk is extremely thin and watery in appearance, and when touched with a platinum needle it can be drawn out into long, slimy threads. The slight acidity which appears during the first three days is perhaps due to the decomposition of certain constituents of the milk fat, for the organism ferments no sugar.

Conclusions.

1. B. *subtilis* and B. *mesentericus* and B. *pyocyaneus* act energetically upon the protein constituents of milk.

2. Their growth in milk is characterized by a noteworthy production of ammonia that is far greater in amount than that produced by the ordinary pathogenic bacteria.

3. The production of ammonia is accompanied by a progressively alkaline reaction in the case of B. *subtilis*, by a transient initial acidity in the case of B. *pyocyaneus*, while B. *mesentericus* produces a progressive acidity.

[1] Kendall and Farmer, *J. Biol. Chem.*, **12**, 215 (1912).

4. *B. pyocyaneus* produces a green coloration in milk even at the end of 24 hrs.

XXXV. The Metabolism of B. Diphtheriae, B. Suipestife Vibrio Cholerae, and B. Tuberculosis in Milk.

One of the diseases which is definitely transmissible by milk 'rom man to man is diphtheria. There are numerous instances on recc 'd where epidemics varying from a few cases to rather extensive outbre ks have been traced definitely to milk supplies. Almost without excep ion the evidence is completed by the discovery on the farm or at som. station where milk has been handled of a case of diphtheria, or a diphtheria carrier has been recognized.

The diphtheria bacillus, however, as appears to be the case for the majority of those organisms progressively pathogenic for man, does not produce deep-seated changes in the medium in which it is growing. A study of the metabolism of the diphtheria bacillus in milk which appears below shows that this organism produces but very little change in the protein constituents of milk, the amount of ammonia formed being but 3.5 mg. per 100 cc. in 14 days. These figures are in close agreement with those obtained by the same organism incubated under parallel conditions in broth.[1] This organism produces, as the tables show, a progressive acidity in milk, the amount of acid produced, however, being comparatively little. This organism ferments dextrose, and it is certain that but at least a portion of this acidity is attributable to the development of acid from the small amount of dextrose-like substance which, as has been stated above,[2] is normally found in fresh milk. Whether any of the acidity produced by this organism is attributable to the liberation of acid phosphates, incidental to the breakdown of casein, or whether it is due to a slight decomposition of milk fats cannot be stated. This organism does not ferment lactose, consequently the acidity observed cannot be attributable to the breakdown of this sugar. The very slight changes in the reaction and composition of milk, as indicated by the tables, show conclusively that this organism could not be detected in milk directly by ordinary chemical procedures.

The bacillus, Swine Plague No. 8, is a member of the hemorrhagic septicemia group pathogenic for swine. It is not an organism which causes noteworthy decomposition of protein. Even in broth containing no sugar, where the conditions for proteolysis are most favorable, this organism has been shown to produce but very little decomposition.[3] It also produces but very little protein breakdown in milk, the maximum amount,

[1] Kendall, Day and Walker, THIS JOURNAL, 35, 1209 (1913)

[2] THIS JOURNAL, Study xxxi. Smith, Theobald, *J. Bact. Soc. Med. Sci.*, 2, 236 (1898).

[3] Kendall, Day and Walker, THIS JOURNAL, 35, 1218 (1913).

TABLE V

Whole milk

Days	Alizarin	Neutral red	Phenolp ith	NH₃ mg increase per 100 cc milk	NH₃ total N₂ per cent
		B diphtheriae			
1	—0 10	+0 10	0 00	1 40	0 23
3	+0 80	+0 20	+0 40	1 40	0 23
7	+1 70	+0 60	+0 30	1 40	0 23
14	+1 00	+0 60	+0 70	3 50	0 56
21	+1 10	+0 50	+1 10	1 40	0 23
		B suipestifer			
1	0 00	+0 20	+0 50	2 10	0 32
3	+0 40	+0 20	+0 70	2 80	0 46
7	—0 80	+0 50	+0 70	2 80	0 46
14	—1 50	—0 10	+0 50	2 80	0 46
21	—1 30	—0 90	+1 10	3 50	0 56

Whole milk

Days	Alizarin	Neutral ed	Phenolphthalein	NH₃ mg increase per 100 cc milk	NH₃ total N₂ per cent
		Vibrio cholerae			
1	+0 40	+0 50	+1 30	—0 70	0 11
3	+0 80	+0 50	+0 70	0 70	0 11[1]
7	+0 10	+0 70	+1 00	0 00	0 00[2]
14	+0 30	+0 30	+0 90	2 10	0 33[2]
21	+1 80	+1 00	+0 90	2.80	0 46[2]
28	+0 90	+0 30	+0 70	1 40	0 23
		B tuberculosis "W"			
1	+0 10	+0 20	+0 20	0 00	0 00
3	—0 10	—0 40	—0 50	7 70	1 23
7	—0 60	—1 80	—1 60	7 70	1 23[2]
14	—0 20	—2 70	—1 70	9 10	1 45[4]
21	—0 80	—1 70	—1 80	11 20	1 80[5]
28	—1 00	—2 20	—1 60	12 60	2 02[5]

[1] Slightly coagulated
[2] Firmly coagulated
[3] Milk brown, somewhat thin
[4] Milk brown, thinner
[5] Milk brown, very thin

3.5 mg., being found on the 21st day. This slight amount of ammonia, which accounts for but 0.56% of the total nitrogen of the milk, is so slight that it would escape detection. There is a slight production of acid which is persistent when phenolphthalein is used as an indicator, but which is replaced by an alkaline reaction when the milk is titrated with alizarin or neutral red as an indicator, the alkalinity disappearing before the 7th day with the former, and between the 7th and 14th days with the latter. The possible sources of this acid are so numerous that no definite statement can be made about it other than that the initial acidity, at least, can logically be attributable to the fermentation of the small amount of dextrose which is apparently a constituent of normal milk. Organisms of the hemorrhagic septicemia group, it should be stated, have never been found in demonstrable numbers in market milk, consequently, this organism has little significance in this medium.

The vibrio of Asiatic cholera has at times been reported as transmissible from man to man through milk. The observations of Hesse[1] would indicate that fresh cows' milk exercises a strong bactericidal action upon cholera vibrios and that this bactericidal action is removed when milk is heated for some time. Prolonged heating, according to Hesse, appears to change milk in such a manner that cholera vibrios no longer grow in it. It is

[1] Hesse, *Z. Hyg.*, **17**, 270 (1894).

generally assumed that this organism finds it way into milk through contaminated water, for the cholera vibrio, so far as is known, is never found in the intestinal tracts of cattle: it is conceivable that the organisms might be introduced into milk by cholera carriers who have the organisms on their hands. A certain amount of presumptive evidence in favor of this view is furnished by the fact that without exception those cases of cholera which appear to have been acquired from drinking milk have occurred in the Orient where the handling of milk is very much less carefully regulated than in more enlightened communities. The cholera vibrio ferments lactose fairly readily and it is not surprising to find a certain amount of acid development in milk. Kitasato,[1] in 1889, showed that the growth of cholera vibrios in milk was associated with an acid reaction. The amount of acid, however, is not very great, but it is sufficient to cause coagulation on the 7th day. The amount of protein breakdown, as indicated by the accumulation of ammonia, is very small indeed· this is in harmony with what has been observed previously[2] when this organism is grown in ordinary broth containing utilizable sugars, the carbohydrate sparing the protein from breakdown. Here again the changes induced in the milk, even when it is kept at body temperature where conditions are apparently optimum for a rapid development of the organisms, are very slight and would absolutely escape detection by ordinary chemical means.

The distribution of tubercle bacilli, particularly bovine tubercle bacilli, in milk is a problem which has been studied for many years. The consensus of opinion at the present time appears to be that occasionally bovine bacilli which enter the intestinal tract of man with milk—particularly young children—may sometimes result in infection. It is assumed, tacitly at least, that these organisms do not develop appreciably in milk, and there are very few references in the literature referring to the effects of their growth in this medium. Klein,[3] however, has shown that the tubercle bacillus may grown fairly rapidly in this medium. *B. Tuberculosis "W.,"* which has been studied in this connection, is an avirulent human tubercle bacillus which grows fairly rapidly on artificial media. It will be observed from an examination of the accompanying table that this organism produces a fair amount of ammonia in milk, amounting to 12.5 mg. per 100 cc. in 28 days. Over half of this ammonia is the end of the third day, indicating that at least the rapidly growing varieties of the organism develop in this medium with moderate luxuriance. The reaction produced is progressively alkaline except for the first 24 hours, when there appears to be a very slight acidity. The degree of alkalinity,

[1] Kitasato, *Z. Hyg.*, **5**, 494 (1889).

[2] Kendall and Farmer, *J Biol Chem.*, **12**, 467 (1912).

[3] Klein, *Cent. Bakt, I Abt.*, **28**, 111 (1900)

however, never becomes very great and a consideration of the metabolism of this strain would indicate that even rapidly growing tubercle bacilli do not produce noteworthy changes in milk At the end of the 7th day the milk appears to be somewhat thinner than normal, and by the end of the third week it is very thin, almost opalescent, resembling in this respect milk in which *B. paratyphosus beta* and *B. icteroides* have been growing. It is very probable that this thinning is due to a decomposition of the casein. Monvoisin[1] has called attention to the milk of tuberculous cattle. His results show that milk drawn from cattle with tuberculous udders very frequently exhibits a hypoacidity and the milk itself is very thin, resembling in composition normal blood serum. It would appear that the changes noticed by Monvoisin are qualitatively somewhat analogous to those noted in the experiments described above, particularly with reference to the increased alkalinity of the milk and the gradual thinning. It is by no means to be assumed, however, that the changes observed by this author are parallel in any sense with those observed in milk infected with a rapidly growing, avirulent, human strain of the tubercle bacillus. Moussu and Monvoisin[2] have studied the composition of milk of tuberculous cows somewhat more extensively than the analyses reported above. They find that in cows with tuberculous udders the acidity of the milk decreases as the disease progresses. There is a decrease in the casein, which has also been shown by Storch. The chlorine content of the milk decreases and the normal acidity is reduced 50% or even 75%. The total nitrogen content is also decreased as well as the fat. These changes, taken in connection with the analyses recorded above, indicate that the tubercle bacillus, grown in milk, and in milk drawn from cows suffering from advanced tuber culosis of the udder, shows a noteworthy diminution in its general composition, these changes being a decrease in acidity, or rather, an increase in alkalinity; a thinning of the milk, and, according to Moussu and Monvoisin, a diminution in the amount of butter fat.

Conclusions.

(1) The diphtheria bacillus produces no visible change in milk even after three weeks' growth at body temperature, and chemically the changes are so slight as to escape detection by ordinary chemical methods.

(2) The cholera vibrio produces an acid coagulation in milk by the end of the which is attributed to the fermentation of the lactose. There is but little coincident protein breakdown, the lactose protecting the milk proteins from degradation.

(3) The rapidly growing, avirulent, human tubercle bacillus grows luxuriantly in milk, producing a moderate breakdown of the proteins and a progressive alkaline reaction. After a week's incubation the milk is

[1] Monvoisin, *Rev. d. Med. Veterin*, 87, 16 (1910); *Compt. rend.*, 21 (1909).

[2] Moussu et Monvoisin, *Compt. rend.*, 62, 26 (1907).

distinctly thinner in consistency and slightly brownish in color. At the end of three weeks the milk is decidedly brownish and almost opalescent.

XXXVI. The Metabolism of Certain Members of the Coccal Group in Milk.

There has been a great deal of discussion regarding the significance of the streptococci found in cows' milk. The most common variety of these, *Streptococcus lacticus*, (Kruse),[1] is culturally very similar to the *Streptococcus pyogenes*, according to Kruse,[1] Heinemann,[2] and others. This organism, together with its numerous variants, appears to be an almost constant inhabitant of ordinary milk, in which medium it usually produces an acid coagulation. Streptococci which are but imperfectly differentiated from *Streptococcus lacticus* are found frequently in the milk drawn from cows with inflammed udders, and epidemics of sore throat, frequently of a severe nature, have also been attributed to streptococci which belong to this same group.

Streptococcus pyogenes grows with moderate luxuriance in milk, producing an acid coagulation of the casein on the third to the seventh day or even earlier, due to the fermentation of lactose. It might be confidently predicted, and the table shows, that there is no considerable coincident breakdown of protein, which is indicated by the relatively slight increase in the ammonia content of the milk even after several days' incubation. Aside from the coagulation which this organism, *Streptococcus pyogenes*, brings about, there is no noticeable change in the composition of the milk, and the changes even when measured quantitatively are very little.

Staphylococcus aureus is much more actively proteolytic than the Streptococcus. This organism ferments lactose as well as other sugars, and it is not surprising to find that the reaction becomes progressively acid, the acidity amounting to 7% at the end of the 14th day. Coagulation is already complete at the end of the third day and there appears to be a certain amount of coincident peptonization which is most marked by the end of the third week. Whether this peptonization is in reality a true liquefaction of the casein coagulum or a contraction of it cannot be stated definitely; from the relatively small amount of ammonia produced, amounting to but 12 mg. in 14 days, it would seem that the proteolytic activity exhibited by this organism, although somewhat greater than that of the Streptococcus, is not sufficient to account for what appears to be a considerable degree of peptonization. The proportionate increase in ammonia formed by the Staphylococcus in milk, as compared with that of the Streptococcus, is in about the same proportion as the ammonia formation by these organisms in broth under the same conditions, and it would appear that the utilization of protein by the Staphylococcus is accompanied

[1] Kruse, *Centr Bakt.*, **34**, 737 (1903).

[2] Heinemann, *J. Inf. Dis.*, **3**, 173 (1906).

by a somewhat deeper-seated change or changes of the protein than is the case when the Streptococcus utilizes the same protein. Whether *Staphylococcus pyogenes aureus* or the chromogenic variants of this organism are to be regarded as pathogenic bacteria occasionally present in milk cannot be definitely stated. This organism usually appears to gain entrance to the tissues of man through abrasions in the skin, or occasionally through damaged mucous membranes. It is quite unlikely, however, that the mucous membrane of the gastro-intestinal tract is a portal of entry for this organism.

TABLE VI

| Days | Whole milk | | | | | Days | Whole milk | | | | |
	Alizarin	Neutral red	Phenolphthalein	NH$_3$ mg per 100 cc milk	NH$_3$ total N: per cent		Alizarin	Neutral red	Phenolphthalein	NH$_3$ mg per 100 cc milk	NH$_3$ total N: per cent
	Streptococcus pyogenes						*Mic zymogenes*				
1	+0 40	—0 30	+0 10	0 00	0 00	1	0 00	+0 80	+2 ?0	2 80	0 44
3	+0 30	—0 20	+0 30	2 10	0 32	3	+1 30	+3 10	+5 40	5 60	0 88[4]
7	+0 30	+0 30	+0 30	1 40	0 22[1]	7	+3 40	+2 50	+6 30	5 60	0 88[4]
14	+0 50	+0 40	+0 50	2 80	0 44[1]	14	+3 30	+3 60	+7 50	8 40	1 32[4]
21	┝0 30	+0 70	+0 60	3 50	0 55[1]	21	+3 30	+3 80	+7 10	8 40	1 32[4]
	Staphylococcus aureus						*Mic melitensis*				
1	+0 30	+0 80	-1 20	2 10	0 32	1	+0 20	+0 10	+0 70	0 70	0 11
3	+2 30	+1 60	+2 80	11 90	1 87[2]	3	+0 10	+0 40	+0 10	1 40	0 22
7	+3.00	+4 70	+6 60	11 90	1 87[2]	7	—0 40	+0 50	+0 50	2 10	0 32
14	+3 40	+5 70	+7 00	12 60	1 98[3]	14	—0 70	+0 50	+0 60	2 80	J 44
21	+3 90	+8 40	+6 80	9 10	1 43[3]	21	—1 50	+0 60	+0 60	3 50	0 55

[1] Coagulation
[2] Coagulation, peptonization slight (?)
[3] Coagulation; peptonization marked
[4] No visible coagulation; peptonization (?).

Micrococcus zymogenes reacts very similarly to *Staphylococcus aureus* in milk, producing in it visible changes which are manifested by a coagulation and separation of serum, by a moderate accumulation of ammonia (amounting to about 9 mg. in 100 cc. of milk), and by a progressively acid reaction which amounts to 7.5% at the end of two weeks. This organism, like *Staphylococcus aureus*, ferments lactose, and the accumulation of acid is, therefore, readily explainable. The comparatively small amount of ammonia formed would speak in favor of the separation of serum as being due to a mechanical contraction of the casein coagulum rather than to an extensive liquefaction of the casein.

Micrococcus melitensis, which is the etiological agent of Malta fever is transmitted to man through the milk of Maltese goats. It is also found in the urine of these animals. Malta fever has recently become endemic

in certain parts of the United States, particularly Texas, where it has been introduced by the importation of goats from the Island of Malta. *Micrococcus melitensis* grows slowly in milk, produces but little ammonia and a slight, progressive acid reaction which is indicated by an increase in the titration values both with phenolphthalein and neutral red. With alizarin as an indicator the reaction after the third day becomes slightly alkaline; the explanation for this phenomenon is not known.

Conclusions.

(1) *Streptococcus pyogenes*, *Staphylococcus aureus*, and *Micrococcus zymogenes* produce an acid coagulation in milk which is visible on the third day; occasionally it may be visible somewhat earlier, and less typically, somewhat later.

(2) The amount of acid formed varies with the organism, *Streptococcus pyogenes* producing relatively little acid, *Staphylococcus pyogenes* and *Micrococcus zymogenes* producing considerable amounts of acid.

(3) *Staphylococcus aureus* and *Micrococcus zymogenes* form somewhat more ammonia than does the *Streptococcus pyogenes* under the same conditions in milk.

(4) Milk cultures of *Staphylococcus aureus* and *Micrococcus zymogenes* exhibit a considerable accumulation of clear serum after coagulation is complete: whether this is to be construed as a true liquefaction of the casein (peptonization), or a mechanical contraction of the casein with the extrusion of whey is not definitely known.

(5) *Micrococcus melitensis* grows slowly in milk, produces no visible change and but very little quantitative change in chemical composition.

XXXVII. The Metabolism of Certain Bacteria in Skimmed Milk, Whole Milk, and Cream.

In a series of previous communications relating to the metabolism of certain bacteria in certified whole milk containing 3.6% butter fat,[1] a number of reactions, chiefly increases in acidity, were encountered, for which no satisfactory explanation could be advanced. The character of these reactions suggested that they might be attributable to the action of these organisms upon some constituent or constituents of the cream, possibly by means of a fat-splitting ferment or lipase. Attempts to study the chemical changes in the cream were temporarily defeated because of the difficulties encountered in obtaining representative samples for analysis.

The observations recorded below were made with a view of determining, grossly at least, the effect of butter fat (cream) upon the metabolism of these bacteria. For this purpose certified skimmed milk (containing 0.15% of butter fat), certified whole milk (containing 3.6% of butter fat), and certified cream (containing 40% of butter fat), prepared in the usual

[1] Kendall, Day, and Walker, "Studies in Bacterial Metabolism, XXXI–XXXVI," inc., This Journal, **36**, 1920 (1914).

manner discussed above, were inoculated under like conditions with certain of these organisms, and these cultures, respectively in skimmed milk, whole milk, and cream, were incubated under parallel conditions and studied at appropriate intervals   The analyses follow

Discussion.

If butter fat exerts any true sparing action for protein, it should be manifested by noteworthy differences in the amounts of ammonia produced when the same organism is grown, respectively, in skimmed milk, containing but little butter fat, and in cream   that is to say, less ammonia would be found in the cream cultures than in the corresponding skimmed milk cultures   The acidity of the cream cultures under these conditions might be confidently predicted to be greater than those in skimmed milk pro vided carbohydrates played no part in the reaction   On the other hand, if the increase in acidity observed in these cultures be due to a fat splitting ferment (a lipase) excreted by the bacteria or liberated from them as the organisms are autolyzed, the cultures should show an increase in acidity without a noteworthy diminution in ammonia production   In other words, a true fermentation of the butter fat[1] might be expected to shield the protein of the milk from bacterial breakdown, precisel as utilizable sugars protect the protein under the same conditions, although perhaps not to the same extent, while, on the contrary, the action of a ferment a lipase in this instance, might be conceived to be more or less independent of proteolysis, in which case the reaction might become progressively acid, although proteolysis progressed normally   It is conceivable that these differences might be masked on the one hand by certain mechanical factors, particularly prominent in cream   for this medium forms a compact layer practically impermeable to air, and it is quite possible that the organisms might, therefore, grow less luxuriantly than would be the case in skimmed milk where access of air is more easily obtained   On the other hand, a resultant acid reaction might be met with even though the proteolysis proceeded normally because the amount of acid produced by the activity of the lipase might be more than sufficient to neutralize the alkalinity of the basic products resulting from the protein breakdown The metabolism of such a culture should show a progressive proteolysis of greater or lesser magnitude associated with a progressive acid reaction

The organisms studied in this connection were *B typhosus*, *B para typhosus alpha* and *beta*, *B coli*, *B proteus*, *B pyocyaneus*, and the avirulent tubercle bacillus "W," all of these organisms being represented in the earlier studies on the subject

B typhosus and *B paratyphosus alpha* and *beta*, as shown in the table, do not exhibit any marked differences in metabolism whether they are

[1] Rubner *Arch Hyg* **38,** 67 (1900) believes that bacteria ferment fats but do not split fats, by lipase action

TABLE VII.

	Skim milk.					Whole milk.					Cream.				
Days.	Alizarin.	Neutral red.	Phenolphthalein.	NH₃ mg. per 100 cc. milk.	NH₃ total N₂ per cent.	Alizarin.	Neutral red.	Phenolphthalein.	NH₃ mg. per 100 cc. milk.	NH₃ total N₂ per cent.	Alizarin.	Neutral red.	Phenolphthalein.	NH₃ mg. per 100 cc. cream.	NH₃ total N₂ per cent.
B. typhosus.															
1	+0.60	+0.50	+0.60	0.70	0.10	+0.20	+0.30	+0.80	0.70	0.11	−0.50	+0.20	−0.40	1.40	0.32
4	+1.10	+1.10	+1.10	2.80	0.40	0.00	+0.80	+1.40	0.70	0.11	0.00	+0.30	+0.70	1.40	0.32
7	+1.20	+0.90	+1.40	1.40	0.20	+0.20	+0.60	+1.40	2.10	0.32	+0.66	+0.20	+0.90	1.40	0.32
14	+2.50	+1.20	+1.20	2.80	0.40	+1.80	+0.70	+1.30	3.50	0.35	+0.66	+0.70	+0.90	2.80	0.64
21	+2.40	+1.20	+1.30	3.50	0.50	+1.60	+0.50	+1.20	4.20	0.64	+0.10	+0.50	+0.80	2.80	0.64
B. paratyphosus alpha.															
1	+0.60	+0.20	+0.50	0.70	0.10	+0.20	+0.40	+0.80	2.10	0.32	+0.10	+0.30	+0.40	0.70	0.16
4	+0.50	+1.20	+1.10	2.10	0.30	+0.10	+1.10	+1.50	2.80	0.44	−0.40	+0.40	+0.30	1.40	0.32
7	+0.50	+0.90	+1.20	2.10	0.30	+0.30	+0.90	+1.50	4.20	0.64	−0.90	+0.80	+0.40	0.70	0.16
14	+1.10	+1.10	+0.90	3.50	0.50	+0.70	+0.70	+1.00	4.20	0.64	−0.60	+0.60	+0.40	1.40	0.32
21	+0.90	+1.00	+0.60	2.10	0.30	+1.20	+0.70	+1.30	4.20	0.64	−0.80	+0.10	+0.20	1.40	0.32
B. paratyphosus beta.															
1	0.00	+0.50	+0.70	0.70	0.10	−0.30	+0.10	+0.60	0.70	0.11	−0.40	+0.20	+0.30	1.40	0.32
4	0.00	−0.20	−0.20	−0.70	0.10	−0.50	−0.60	−0.30	0.00	0.00	−0.90	0.00	+0.40	0.70	0.16
7	−0.10	−1.40	−1.90	1.40	0.20	−0.00	−2.00	−1.40	0.70	0.11	−1.30	−1.30	−0.66	0.00	0.00
14	−1.20	−2.00	−1.70	2.80	0.40	−1.40	−3.40	−1.20	1.40	0.22	−1.70	−1.80	−0.80	0.70	0.16
21	−0.80	−3.70	−1.90	5.60	0.80	−0.50	−1.90	−1.40	2.80	0.44	−0.80	−1.30	−0.90	2.10	0.48

B coli

Day															
1	+0 40	+3 40	+4 60	-0 70	-0 10	0 00	+3 20	+4 80	0 00	0 00	+0 90	+1 40	+2 40	-0 70	-0 16
4	+1 50	+3 60	+5 10	-1 40	-0 20	+0 80	+3 30	+4 40	0 00	0 00	+0 80	+2 20	+2 10	-0 70	-0 16
7	+3 10	+5 10	+5 60	0 00	0 10	+1 90	+4 10	+5 20	0 00	0 00	+0 60	+2 10	+2 80	0 00	0 00
14	+3 70	+5 50	+5 70	+0 70	0 10	+2 90	+4 50	+5 10	0 70	0 11	+0 70	+3 00	+3 00	+0 70	0 16
21	+3 80	+5 80	+6 00	+1 40	0 20	+3 10	+4 60	+5 30	1 40	0 22	+1 40	+3 30	+3 20	+1 40	0 32

B proteus

Day															
1	+0 30	+0 60	+1 00	8 40	1 20	-0 70	+0 30	+1 70	11 90	1 87	-0 10	+0 50	+0 90	4 20	0 95
4	+1 20	+1 30	+3 10	18 90	2 70	+0 60	+1 10	+2 90	21 00	3 30	+0 50	+0 66	+1 60	11 20	2 54
7	+1 80	+5 70	+4 40	24 50	3 50	+0 50	+2 20	+4 30	26 60	4 18	+0 90	+0 80	+2 40	14 00	3 18
14	+1 20	+5 60	+5 60	28 70	4 10	+0 30	+2 10	+5 20	31 50	4 95	+1 00	+0 90	+2 90	39 20	8 90
21	+1 00	+5 20	+5 60	32 20	4 60	+1 40	+1 00	+5 30	33 60	5 28	+0 90	+1 00	+3 70	61 60	14 00

B pyocyaneus

Day															
1	+0 80	-0 20	+0 10	-1 40	-0 28	0 00	-0 10	+0 40	0 00	0 00	-1 60	+0 30	+0 30	0 70	0 16
4				11 90	1 70				14 00	2 20	+1 90	-0 10	+0 40	2 10	0 48
7	-1 30	-1 00	-2 70	35 70	5 10	+2 30	-4 50	+3 30	67 90	10 65	+1 40	-2 20	+2 80	18 90	4 29
14	-1 30	-3 70	-2 80	151 90	22 70	+2 30	-5 80	-2 80	137 20	21 50	+2 50	-2 60	+1 30	50 40	11 40
21	-0 60	-3 60	-2 70	154 70	22 10	+2 20	-6 40	-2 70	154 70	24 40	+2 10	-3 40	+0 50	72 10	16 30

B tuberculosis "W"

Day															
1	+0 66	+0 66	+0 20	1 40	0 20	+0 10	+0 10	+0 10	1 40	0 22	-1 20	+0 10	-0 10	0 70	0 16
4	-0 70	-1 40	-1 30	7 00	1 00	+0 50	+0 50	+0 40	10 50	1 65	-0 80	-0 10	-0 10	2 80	0 64
7	-1 10	-1 70	-1 80	0 10	1 30	-1 20	-1 30	-0 80	20	1 76	-0 20	-0 20	-0 20	3 50	0 80
14	-0 59	-1 90	-1 80	11 90	1 70	-0 60	-1 80	-1 10	13 30	2 09	+0 40	0 00	-0 70	7 70	1 74
21	0 00	-1 90	-2 30	12 60	1 80	0 00	-1 70	-1 80	11 20	1 76	+0 50	-0 30	-0 90	6 30	1 43

developed in skimmed milk, whole milk, or cream. The amount of protein breakdown recorded in percentage is about the same for each of these organisms in each of the media.

B. typhosus and *B. paratyphosus alpha* produce a permanent acid reaction in skimmed milk as well as in whole milk. It will be remembered that an acid reaction was produced by these organisms in whole milk in the above-mentioned studies.[1] The growth of these organisms in these media furnishes no definite explanation for this acid reaction.

B. paratyphosus beta, similarly, exhibits an initial acidity, which, however, is followed by an alkaline reaction. It is apparent that the variation in composition of the media has not influenced, in any noteworthy manner, either the nature or the extent of the metabolism of these three organisms.

B. coli does not exhibit any noteworthy differences in metabolism in the three media, although the reaction produced is somewhat more acid than it is in either whole milk or cream. The amount of ammonia, however, formed in skimmed milk does not differ materially from that observed in whole milk or cream, and, aside from the slight difference in reaction noted, the organism appears to thrive equally well in the three media, producing in them changes of about the same magnitude.

B. proteus forms more ammonia both relatively and absolutely in cream than it does in either skimmed milk or whole milk. This organism, it will be remembered, does not ferment lactose; consequently, this sugar cannot exert any sparing action for the protein constituents of milk and cannot have any part in the production of acid in milk. Why the protein content of cream should undergo a greater decomposition than the protein of skimmed or whole milk is not readily explainable. Notwithstanding the increase of proteolysis in cream as contrasted with that observed in skimmed or whole milk, *B. proteus* effects a noteworthy decomposition of protein in either instance, amounting to 33 mg. of ammonia in the milk containing less butter fat, and to about 60 mg. of ammonia in the cream. The reaction is somewhat less acid in cream, prob ably due, in part at least, to the proportionately greater accumulation of ammonia. It is difficult to explain the acid reaction produced by this organism on the basis of information contained in the tables.

B. pyocyaneus appears to act less energetically upon the proteins in the cream media than the proteins contained in whole or skimmed milk. There is associated with this restriction of proteolysis, amounting to about 50%, a progressively acid reaction to phenolphthalein in cream. Reactions to alizarin and neutral red are less accurate, for the color change induced in the milk as the result of the growth of *B. pyocyaneus* obscures the end point and makes the titrations less accurate. The noteworthy

difference in reaction observed in cream as compared with skimmed and whole milk would appear to rule out the possibility of a restricted growth of the organism in cream as a possible explanation for the decrease in proteolysis This reaction reaches a maximum corresponding to 2 8% acid on the 7th day, and then decreases as ammonia formation proceeds Remembering that *B pyocyaneus* ferments no sugars this acid reaction, which appears during the initial stages of development of the organism in cream and also in skimmed and whole milk before proteolysis has pro gressed to any considerable degree, would lead to the plausible assumption that this acidity may be due, partially at least, to a fat splitting ferment Sommaruga[1] has shown that both *B typhosus* and *B pyocyaneus* produce lipases in gelatin and agar media containing oil or fats The decrease in acidity after the first week may, perhaps, be due to the gradual accumu lation of ammonia, ammonia formation progressing rapidly at this time It is stated by Michaelis[2] that alkalies tend to inhibit the action of lipases of vegetable origin

The avirulent, rapidly growing, human tubercle bacillus W" shows no noteworthy differences in metabolism or reaction when it is grown, respectively, in skimmed milk, whole milk, and cream It should be ob served, however, that the reaction in cream is less alkaline than is the case in either skimmed milk or whole milk Whether lipases play any part in this reaction or not cannot be stated definitely The organism produces a moderate amount of breakdown of the proteins of the three media respectively, and the results obtained in whole milk correspond closely with those recorded in the previous experiment in the same media [3]

Conclusions.

(1) *B typhosus, B paratyphosus alpha* and *beta, B coli,* and the tubercle bacillus ' W" do not exhibit any marked differences in their nitrogen metabolism as measured by ammonia formation, or in their reactions to various indicators when they are grown under similar conditions in whole milk, skimmed milk and cream

(2) The permanent acid reaction, which is a feature of the growth of *B typhosus* and *B paratyphosus alpha,* in whole milk, is also produced in skimmed milk and cream The initial acidity followed by an alkalinity, which is a characteristic of *B typhosus* and *B paratyphosus beta* in milk is also observed in cream

(3) *B proteus* is more proteolytic in cream than it is in whole milk or skimmed milk

[1] Sommaruga Z Hyg , **18,** 454 (1894)

[2] Michaelis Abderhalden's "Handbuch d biochem Arbeitsmethoden Vol III, p 23

[3] Kendall, Day and Walker, 'Studies in Bacterial Metabolism, XXXV ' THIS JOURNAL **36,** 1933 (1914)

(4) *B. pyocyaneus* is less proteolytic in cream than it is in whole milk or skimmed milk.

(5) The presence of certain pathological bacteria, *B. typhosus*, and *B. paratyphosus alpha* and *beta*, cannot be detected in milk by the chemical changes which they induce in it.

CHICAGO, ILL.

STUDIES IN BACTERIAL METABOLISM.

BY ARTHUR I. KENDALL, ALEXANDER A. DAY AND ARTHUR W. WALKER.

XXXVIII. Observations on Fat-Splitting in Milk by Bacterial Lipase.

A study of the metabolism of certain bacteria in sterile whole milk disclosed certain reactions, chiefly relating to the production of titratable acid in the presence of the progressive formation of basic products of protein breakdown, which could not be explained by any available information. *B. typhosus* and *B. paratyphosus alpha*, for example, produced a progressively acid reaction in milk, while *B. paratyphosus beta*, an organism very closely related, both qualitatively and quantitatively, produced a terminal alkalinity in the same medium under the same conditions. Similarly, *B. proteus* and *B. mesentericus* produced a progressive acid reaction, while *B. subtilis* produced a progressively alkaline reaction, notwithstanding the fact that all three organisms are strongly proteolytic. Several possibilities present themselves to explain these results:

(1) It might be assumed that there is a liberation of phosphoric acid, probably as acid phosphates, during the course of the bacterial digestion.

(2) The fermentation of fats in the Rubner sense,[1] with the liberation of fatty acids from the cream, might be a possibility.

(3) These organisms may secrete lipases, which break down the fatty constituents of the milk, perhaps independently of the protein metabolism.

(4) Other causes, as, for example, the possible formation of acid-reacting products, the result of protein decomposition.

There is no direct evidence for any of these assumptions, so far as these studies have shown: there is a certain amount of *à priori* objection to possibilities 1, 2, and 4, chiefly theoretical, however, and due to imperfect knowledge of the nature of intermediary metabolism of bacteria. To assume the presence of a fat-splitting ferment would appear to be a most logical hypothesis to consider first, and with this possibility in view the following experiments were made:

Broth cultures of *B. typhosus*, *B. coli*, *B. proteus*, *B. subtilis*, *B. mesen-*

[1] Rubner, *Arch. Hyg.*, **38**, 67 (1900).

tericus, and *B. pyocyaneus*, respectively, in plain and dextrose broth were grown for ten days at 37° then filtered through Berkefeld filters to separate out the bacteria. Plain and dextrose broths were chosen because the products formed by all the organisms, except *B. subtilis*, and probably *B. pyocyaneus*, are widely different in the two media.[1] There is, furthermore, apparently about 0.1% dextrose in good grades of milk, an amount which the dextrose-fermenting organisms can soon use up, however, forcing them then to utilize other substances in their dietary.[2]

TABLE I
Filtrate.
Cc 0 02 N NaOH

	Cream				Ethyl butyrate		Triacetin	
	Neutralize start	24 hours	Neutralize start	24 hours	Neutralize start	24 hours	Neutralize start	24 hours
Plain broth								
B *typhosus*	+0 90	0 00	+0 80	0 00	+0 10	0 00	+0 50	+1 25
B *coli*	+0 80	+0 05	+0 70	0 00	+0 20	0·00	+0 45	+1 15
B *proteus*	+0.20	0 00	+0 20	0 00	—0 75	0 00	—0 10	+0 85
B *subtilis*	+0 55	0 00	+0 65	0 00	+0 20	0 00	+0 40	+1 10
B *mesentericus*	+1 15	+0 25	+1 25	+0 25	+0 50	+0 05	+0 60	+1 30
B *pyocyaneus*	+0 15	0 00	+0 20	0 00	—0 50	+0 10	+0 15	+0 70

Cc 0 02 N NaOH
Dextrose broth

	Cream				Ethyl butyrate		Triacetin	
B *typhosus*	+2 70	+0 10	+2 90	+0 15	+1 65	+0 30	+2 10	+1 30
B *coli*	+2 80	+0 05	+3 00	+0 05	+2 35	+0 15	+2 50	+1 10
B. *proteus*	+2 85	+0 20	+3 00	+0 20	+2 25	+0 35	+2 40	+1 30
B *subtilis*	+0 30	0 00	+0 35	0 00	+0 45	0 00	+0 60	+1 35
B *mesentericus*	+2 10	+0 20	+2 20	+0 20	+1 65	+0 25	+1 70	+1 15
B *pyocyaneus*	+0 40	+0 20	+0 35	+0 25	—0 45	+0 10	+0 20	+0 95

Bacteria
Cc 0 02 N NaOH

	Cream				Ethyl butyrate		Triacetin	
B *typhosus*	+0 55	+0 25	+0 60	+0 20	0 00	+0 15	+0 30	+0 60
B *coli*	+0 45	+0 15	+0 50	+0 15	—0 15	+0 15	+0 35	+0 80
B *proteus*	+0 60	+0 40	+0 45	+0 45	—0 15	+0 30	+0 40	+1 15
B *subtilis*	+0 60	+0 25	+0 65	+0 30	+0 10	+0 15	+0 50	+1 00
B *mesentericus*	+0 50	+0 40	+0 40	+0 30	+0 10	+0 25	+0 40	+1 10
B *pyocyaneus*	+0 60	+0 35	+0 55	+0 30	+0 05	+0 15	+0 40	+1 00

Controls
Cc 0 02 N NaOH

	Cream				Ethyl butyrate		Triacetin	
B *typhosus*	+0 50	0 00	0 00	0 00	+0 10	+0 05		

[1] Kendall, Day and Walker, THIS JOURNAL, **35**, 1243 (1913)

[2] Kendall, Day and Walker, "Studies in Bacterial Metabolism, XXXI," THIS Journal, **36**, 1920 (1914)

The details of the technique used in testing lipolytic activity of bacterial growth have been described in detail elsewhere[1] and will not be referred to here other than to mention the general procedure.

One cc. of the sterile filtrate was introduced into large, clean test tubes containing toluol water (10 cc.). It will be seen that, theoretically at least, but $1/100$ of the total reactive substance of the original culture is thus brought under observation, for the initial volume of each culture was uniformly 100 cc. To these diluted cultures 0.25 cc. neutral ethyl butyrate and triacetin, respectively, were added, and the whole thoroughly mixed by vigorous shaking, neutralized to phenolphthalein with 0.02 N NaOH or HCl, as the reaction warranted, and incubated at 37° for 24 hours. The increase in acidity is taken as a measure of the esterase activity of the solution in which the determination was made. Appropriate controls, using sterile (uninoculated) media of like kind and amount with ester, and ester controls in water, were made at the same time, and inoculated under the same conditions. These controls were uniformly negative, that is, they did not break down the esters, indicating clearly that the reactive substance is present only in the filtrates of the cultures.

To determine the action of these filtrates in cream, 1 cc. of 40% certified cream was sterilized in the autoclave, after the addition of 10 cc. of distilled water. One cc. of the respective filtrates were added to this sterile, diluted cream, together with toluol, and examined according to the same procedure with suitable controls.

The results follow: Table VIII shows the amount of 0.02 N NaOH required to neutralize the acid liberated from the ester, the glyceride and the cream (duplicate), respectively, as these substances were acted upon by the sterile filtrates of the organisms mentioned above. For the sake of completeness, the initial neutralizing values are given, which indicate the amounts of acid or alkali necessary to bring the mixtures of filtrate and ester to neutrality prior to incubation.

Discussion.

B. mesentericus appears to be the only organism which elaborates a reactive substance (lipase) in plain broth, which forms acid by breaking down the glycerides in the cream. None of the plain broth filtrates of the various organisms appear to liberate acid from ethyl butyrate, while all act to a considerable extent on triacetin. Grown in dextrose broth, the filtrates of all the organisms, except *B. coli* and *B. subtilis*, produce a certain amount of acid in cream after 24 hours, *B. typhosus* somewhat less than the remaining bacteria. *B. typhosus*, *B. proteus* and *B. mesentericus* filtrates (dextrose) act more energetically than the other organisms on ethyl butyrate, while all the types studied liberate consider-

[1] Kendall, Walker and Day, to appear in *J. of Infectious Diseases, November, 1914*.

able amounts of acid from triacetin, as was the case with the plain broth filtrates. It will be seen from Table VIII that the filtrates of those bacteria which ferment dextrose are more active lipolytically than the corresponding plain broth filtrates. This may be attributable, in part at least, to the greater luxuriance of growth in dextrose bioth. These results do not fully meet the requirements of the hypothesis, however, for it is conceivable that those bacteria whose filtrates do not exhibit any appreciable action on the cream might still contain within their bodies an endo-ferment, which was not present in the culture media separated from them by filtration through porcelain.

To examine this possibility, the organisms mentioned above were inoculated upon slanted plain nutrient agar, the area of which was about 50 sq. cm. per organism. The bacteria were washed from the agar after three days' incubation at $37°$ with 5 cc. of sterile toluol water. This killed the organisms. The suspension was then thoroughly shaken to distribute the bacteria uniformly, and 1 cc. of this suspension of dead organisms was added to the cream (in duplicate), ethyl butyrate and triacetin, respectively, as outlined above. The reaction was adjusted to the neutral point of phenolphthalein, then incubated at $37°$ for 24 hours.

The results appear in Table VIII. All the organisms, except *B. mesentericus*, produced more acid in cream than did the filtrates of the broth cultures, either plain or dextrose. The killed culture of *B. mesentericus* liberated no more acid from cream than did the dextrose filtrate. The killed culture of *B. proteus* was about as active as the killed culture of *B. mesentericus* in cream, and both these organisms exhibited greater lipolytic activity than the remaining bacteria. Generally speaking, the less proteolytic bacteria of this series are less active lipolytically, particularly in cream.

It has been claimed that the butter fat of milk is an emulsion of extremely finely divided fat droplets, each droplet being encased in a protein-like envelope. The possibility presents itself, therefore, that the actively proteolytic bacteria may have produced, parallel with the lipase, an exo-proteolytic ferment, and that this ferment may have dissolved the protein-like envelope, exposing the fat to the direct action of the lipase. The sterile filtrates of the broth cultures (plain and dextrose) of the various organisms, consequently, were tested for an exo-proteolytic ferment, using carbol gelatin (0.50% carbolic acid, 8% gelatin) as a substrate, 1 cc. of the dextrose and plain broth filtrates, respectively, being added to a column of this (sterile) carbol gelatin whose dimensions were 60 × 15 mm., and incubated at $37°$ for two days. The results follow:

	LIQUEFACTION	
	Plain broth	Dextrose broth
B. typhosus	..	. .
B. coli ..	. ..	. .
B. proteus	Complete	. .
B. mesentericus	Complete	
B pyocyaneus		Complete

It will be observed that *B. proteus* and *B. mesentericus*, which ferment dextrose, produced no demonstrable gelatinase in dextrose broth, while in plain broth (of precisely the same composition and reaction, except for the dextrose) a very active gelatinase was demonstrable. This suggests strongly that the sparing action of dextrose for protein also influences the production of proteolytic ferment.[1] The production of an active gelatinase by *B. proteus, mesentericus,* and *pyocyaneus* in filtrates of broth cultures simultaneously with active lipases would appear to warrant the tentative assumption that these proteolytic ferments might dissolve the protein-like envelope surrounding the droplets of fat, thus facilitating the lipolytic splitting of this fat.

Conclusions.

(1) The sterile filtrates of broth cultures of certain bacteria split certain esters and glycerides with the liberation of acid.

(2) Generally speaking, the filtrates of dextrose broth cultures of these organisms are more active than the corresponding plain broth filtrates.

(3) This increased activity of the dextrose filtrates may be attributable, in part at least, to the greater luxuriance of growth of the bacteria in this medium.

(4) Autolyzed killed cultures of the same ·bacteria also split esters and fats; and absolute measure of the respective lipolytic activity of the filtrates and bacteria, is not available.

(5) Certain proteolytic bacteria, *B. proteus, B. mesentericus,* and *B. pyocyaneus* appear to split cream somewhat more actively than the less proteolytic organisms. They produce a soluble, active gelatinase in media containing no utilizable carbohydrate.

(6) The presence of this gelatinase in cultures containing active lipase appears to be associated with a more extensive liberation of acid from butter fat (cream), but not from ethyl butyrate and triacetin.

(7) The extent of the splitting of ethyl butyrate and triacetin by all the bacteria studied (both filtrates and killed organisms) appears to be independent of their relative proteolytic activity.

CHICAGO, ILL   ·

[1] Kendall, *Boston Med. and Surg J*, **163,** 322 (1910), *J Med Research,* **25,** 117 (1911)

NOTE.

A Device to Aid in Freeing a Precipitate from Mother Liquor when Filtering by Suction.—In using a Büchner funnel and filtering by suction, it often happens that cracks will form in a bulky precipitate and break the vacuum. Even if the precipitate is fairly compact it is often difficult to remove a very considerable part of the mother liquor. Both of these difficulties may easily be obviated if, after the precipitate appears fairly dry on the filter, one fastens over the top of the Büchner funnel a piece of thin sheet rubber, held in place by a rubber band. The suction within the flask draws the rubber down until it presses firmly over the sides of the funnel and over the top of the precipitate. The efficiency of this method may be noted by the renewed dropping of liquid from the funnel. The surface of the rubber may now be tightly pressed with a pestle or with the hand without fear of either breaking the filter paper beneath or of contaminating the precipitate.

I find that one can easily get a pressure equivalent to 745 mm. of mercury when the barometer stands at 760 mm., and that under such pressure a precipitate becomes as dry—or drier—than it would be if it were removed from the funnel, folded in cloth, and pressed in a "beef-juice" press. The sheet rubber can be easily washed and used repeatedly.

<div style="text-align:right">Ross Aiken Gortner.</div>

Div of Soils, Univ. Farm,
St Paul, Minn.

NEW BOOKS.

Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological. Published under the auspices of the International Association of Academies and under the direction of an international commission appointed by the VII International Congress of Applied Chemistry Volume III, for the year 1912, LII + 595 pp Chicago University of Chicago Press, 1914. Price, paper, $6.40 net, $6.94 postpaid; cloth bound, $7 20 net, $7.76 postpaid.

The third volume of these indispensable tables exhibits several features not found in the previous volumes. In certain chapters alphabetical lists of substances for which data are recorded add to the convenience of the tables. A general index of technical substances for the whole volume has also been added. For every five volumes it is proposed to publish a general index of all substances for which data of any kind are recorded. The following chapters of the present volume have been issued also in the form of separates: Spectroscopy, radioactivity, electricity, magnetism and electrochemistry, metallurgy and engineering, mineralogy, and biology. At the end of Volume III tables of errata for the first three volumes are presented. Attention may be called again to the importance of notifying the editor of errors in each volume. Postal cards for this purpose are bound with each volume. Every investigator should make it his duty to

verify the record of all data determined by him and to notify the editor of any errors which appear.

The war in Europe can not fail to interfere with all international undertakings of the character of these tables and upon the countries not directly involved, and especially upon this country, will fall the duty of carrying on this work without interruption. The chemical and physical societies of American should increase as much as possible their financial support to this extremely important work and should take all necessary steps to prevent its interruption. It is to be hoped that the Secretary's office will be removed as soon as possible to a neutral country whose mail service can be depended upon and that he will receive all the support, financial and otherwise, which the present crisis renders necessary.

E. W. WASHBURN.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

THE FREE ENERGY OF OXYGEN, HYDROGEN, AND THE OXIDES OF HYDROGEN.[1]

By Gilbert N. Lewis and Merle Randall

Elementary Oxygen.[2]

The standard state of oxygen will be gaseous oxygen at a pressure of one atmosphere. We might proceed from existing data to calculate the free energy of liquid and solid oxygen, but since the required data are still somewhat uncertain, and since these calculations must be pretty exact to be of value, we shall postpone the calculation of the free energy of oxygen and hydrogen in the liquid and solid state until further data are at hand.

Oxygen unquestionably dissociates, at the high temperatures which are now available, into monatomic molecules, but, as yet, no quantitative

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[1] This is the first of a series of papers in which the free energy of formation of the more important compounds will be calculated and tabulated.

[2] It is perhaps impossible to prepare such tables as these without permitting some errors to creep in, but every precaution which might serve to eliminate such errors has been taken; the experimental data have been most carefully scrutinized in order to determine not only the most probable value in each case, but also the order of magnitude of the possible error. As a rule, however, this estimate of error has been indicated only by the number of significant figures used. As a safeguard against error in computation every calculation has been carried on independently by the two authors.

measurements are at hand for the calculation of the free energy of this important reaction.

$3/2\ O_2 = O_3$.—The heat capacity of ozone has not been accurately determined. We shall, however, make no great error in assuming that the equation which holds for the two triatomic gases,[1] CO_2 and SO_2, is applicable in this case also, namely:

$$O_3;\ C_p = 7.0 + 0.0071T - 0.00000186T^2 \qquad (1)$$

from which we may subtract the heat capacity of $3/2$ mols of oxygen from the equation

$$O_2;\ C_p = 6.50 + 0.0010T,$$

whence

$$\Delta\Gamma = -2.75 + 0.0056T - 0.00000186T^2 \qquad (2)$$

and[2]

$$\Delta H = \Delta H_0 - 2.75T + 0.0028T^2 - 0.00000062T^3 \qquad (3)$$

The heat of this reaction has been determined by a number of investigators, who have obtained values for ΔH ranging from 23000 to 36000 cal. These results are fully discussed in Ostwald's "Lehrbuch." We will take 34000 cal. as the most probable value. Hence

$$\Delta H = 34600 - 2.75T + 0.0028T^2 - 0.00000062T^3 \qquad (4)$$

and

$$\Delta F^\circ = 34600 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + IT \qquad (5)$$

The attempts to study the free energy of this reaction have achieved little success. The potential of the ozone electrode has been studied, especially by Luther and Inglis,[3] who obtained nearly reproducible potentials by means of a platinum electrode surrounded by ozone, but they were unable to determine definitely the nature of the electrode reaction, and, in fact, it was later shown by Luther[4] that, with an iridium electrode, values differing from those with the platinum electrode by as much as 0.2 volt could be obtained.

The numerous unsuccessful attempts to detect ozone in oxygen suddenly cooled from a high temperature were shown by Clement[5] to be due to the extremely rapid rate of decomposition of ozone even at comparatively low temperatures. Later Fischer and Braehmer[6] succeeded in obtaining ozone by heating a filament to about $2300°$ A under liquid oxygen. If we admit the validity of certain assumptions suggested by Fischer and Braehmer, which, however, at best could be only very roughly true,

[1] Lewis and Randall, This Journal, **34**, 1128 (1912).

[2] For a discussion of the fundamental equations and notation see Lewis, Ibid., **35**, 1 (1913).

[3] Luther and Inglis, Z. physik. Chem., **43**, 203 (1903).

[4] Luther, Z. Elektrochem., **11**, 832 (1905).

[5] Clement, Ann. Physik., [4] **14**, 334 (1904).

[6] Fischer and Braehmer, Ber., **39**, 940 (1906).

the oxygen at the temperature of the filament contained one mol per cent. of ozone, whence $K = p_{O_2}/(p_{O_3})^{1/2} = 0.01$; and if R' is the gas constant in calories per degree, $\Delta F°_{2300} = -R'T \ln K = 21000$ cals. Substituting in (5) gives $I = -22.4$, whence $\Delta F°_{298} = 32400$.

It is, however, doubtful whether even the order of magnitude of the equilibrium constant between oxygen and ozone can be safely estimated from the data here employed.

Elementary Hydrogen.

We shall take ordinary gaseous hydrogen at a pressure of one atmosphere as the standard state. The only reaction, involving only elementary hydrogen, which we shall consider here is the very interesting reaction investigated by Langmuir.[1]

$H_2 = 2H$.- Langmuir's measurements of the equilibrium in this reaction between 2500°A and 3300°A depended upon a highly ingenious and novel method of calculation which is apparently correct in principle, but involves certain assumptions which his later work[2] have shown to be in some respects erroneous. In his first paper he calculated the heat of this reaction as -136000 cal., and the degree of dissociation of hydrogen at one atmosphere as 0.04 at 2500°A. Dr. Langmuir has been kind enough to give us the results of a preliminary calculation of his new data, which give the degree of dissociation at 2500°A as about 0.01, and the heat of the reaction as between -54000 and -75000 cal., the most probable value being in the neighborhood of -64000, which is the value obtained theoretically by Bohr[3] from his hypothesis concerning the structure of atoms.

We know little concerning specific heats at these high temperatures, but shall assume, as at lower temperatures,[4] that

$$H_2;\ C_p = 6.5 + 0.0009T$$
$$H;\ C_p = 5.0$$

Hence for the total increase in heat capacity

$$\Delta\Gamma = 3.5 - 0.0009T. \tag{6}$$

And, assuming ΔH_{2500} to be 64000,

$$\Delta F° = 61000 - 3.5T \ln T + 0.00045T^2 + 20.2T, \tag{7}$$

where the value of $I = 20.2$ is obtained as follows: At 2500°A, if the pressure of H_2 is one atmosphere, and of H, 0.01 atmosphere, $K = 0.0001$ and $\Delta F°_{2500} = -R'T \ln K = 45800$; and thence $I = 20.2$, and $\Delta F°_{298} = 61100$.

The determination of the dissociation of elementary gases into the

[1] Langmuir, THIS JOURNAL, **34**, 860 (1912). ·
[2] Langmuir, *Phil. Mag.*, **27**, 188 (1914).
[3] Bohr, *Ibid.*, **26**, 857 (1913).
[4] Lewis and Randall, THIS JOURNAL, **34**, 1128 (1912).

monatomic forms is of the greatest importance. If we could use as the standard state of each element its monatomic gas at standard pressure, this would probably be a most important step towards the theoretical calculation of the thermodynamically undetermined constants of chemical affinity.

Hydrogen Ion.

$1/2 H_2 + \oplus = H^+$. — Hydrogen ion in water is doubtless largely hydrated. While the hydronium ion OH_3^+ is presumably less stable under similar circumstances than the corresponding ammonium ion NH_4^+, it probably exists in considerable amount, together with higher hydrates of hydrogen ion, in every aqueous acid solution. For the purpose of such thermodynamic calculations as we are about to make, it is justifiable to assume the simplest formula for hydrogen ion, namely, H^+, and the formation of this ion in aqueous solution will be represented by the above equation.

The value of ΔF° for this reaction will be understood to be the increase in free energy when one-half mol of hydrogen, at atmospheric pressure, and one equivalent of positive electricity disappear, and one mol of hydrogen ion appears in aqueous solution at (hypothetical) molal concentration.[1] Now, since it is impossible at present to determine the absolute free energy change in any such "half reaction," it has seemed desirable[2] to regard the normal free energy change of this particular half reaction as zero at all temperatures.

$$1/2 H_2 + \oplus = H^+; \quad \Delta F^\circ = 0 \text{ (all temperatures)} \qquad (8)$$
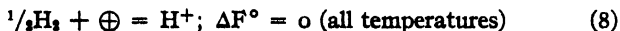
This is equivalent to the convention that for the normal electrode potential of hydrogen,

$$E^\circ = 0 \text{ (all temperatures)} \qquad (9)$$

Hydrogen and Calomel Electrodes.

Since we are to take the normal potential of the hydrogen electrode as the arbitrary zero of single potential, and refer all other single potentials to it, it is desirable to know accurately the relation between this standard electrode and others which are in common use. The older work on the hydrogen electrode by Smale, Wilsmore and others[3] has been superseded by work of the last few years. We shall refer especially to the papers of Bjerrum,[4] Lorenz and Böhi,[5] Loomis and Acree,[6] and to an unpublished

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[1] A solution is said to be at (hypothetical) molal concentration with respect to hydrogen ion when the activity of hydrogen ion in this solution is n times as great as in a $1/n$ M solution of hydrogen ion, where n is a large number.

[2] Lewis, THIS JOURNAL, **35**, 25 (1913).

[3] See Wilsmore, Z. physik. Chem., **35**, 291 (1900).

[4] Bjerrum, Ibid., **53**, 430 (1905).

[5] Lorenz and Böhi, Ibid., **66**, 733 (1909).

[6] Loomis and Acree, Am. Chem. J., **46**, 585 (1911).

investigation of Lewis which was interrupted several years ago and has never been completed. However, a number of accurate measurements were made of the hydrogen potential at different temperatures and pressures, and in acid and alkaline solutions, and the results will be given here.

The most important measurements for our purpose are those which have been made in $0.1M$ HCl against a calomel electrode in $0.1M$ KCl or $0.1M$ HCl. In the latter case there is no liquid potential.

The cell H_2, HCl ($0.1M$), KCl ($0.1M$), HgCl, Hg gives, according to Bjerrum, $E = 0.4270$ volt at $25°$. At the same temperature Loomis and Acree find $E = 0.4266$. In order to compare these values with those obtained against the $0.1M$ HCl calomel electrode it is necessary to know the e. m. f. of the cell Hg, HgCl, KCl ($0.1M$), HCl ($0.1M$), HgCl, Hg. If we assume, what is undoubtedly very nearly true, that the two single electrode potentials in this combination have the same value,[1] then the whole electromotive force of this cell is the potential between the liquids. This liquid potential calculated by the formula of Lewis and Sargent is -0.0284 volt.[2] Bjerrum[3] has studied the electromotive force of this combination and finds, as Lewis and Rupert also found, that the liquid potential changes with the time. He showed, moreover, that different values were obtained according to the way in which the contact between the two liquids was made. His best value was $E = -0.0278$ volt. The values obtained by Lewis for this combination were, however, near the theoretical value -0.0284 volt, and this is the value we shall adopt for the present.[4]

By adding together the values of E obtained for the two cells, we find for the combination H_2, HCl ($0.1M$), HgCl, Hg; $E = 0.3986$ (Bjerrum), and 0.3982 (Loomis and Acree). Lewis found, as a mean of several direct determinations, 0.3987 at $25°$.[5] The mean of these values is $E = 0.3985$. In all of these cases the hydrogen was not at atmospheric pressure, but at one atmosphere less the pressure of water vapor at $25°$. We must,

[1] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[2] See Lewis and Rupert, *Ibid.*, **33**, 299 (1911). The value obtained by the unmodified formula of Planck, -0.0266, is unquestionably erroneous.

[3] Bjerrum, *Z. Electrochem.*, **17**, 61 (1911).

[4] Since this paper was first written the hydrogen electrode potential has been very carefully investigated in this laboratory by Mr. Sebastian His work is to be published shortly. In the meantime we have rewritten certain sections of this paper in order to include some of his results. His value for the e. m. f. between calomel electrodes in $0.1 M$ KCl and $0.1 M$ HCl is identical with the value chosen above, -0.0284

[5] Loomis and Acree also measured this cell directly and obtained $= 0.4001$, but they regarded these as preliminary measurements and we need give them no weight. Their discussion of the liquid potentials calculated by the formula of Lewis and Sargent is erroneous in that they have confused certain conductivity values at $18°$ with values at $25°$.

therefore, make a correction of the magnitude $\dfrac{RT}{2F} \ln \dfrac{1}{p}$ where p is the actual pressure of the hydrogen in atmospheres and R is the gas constant in joules per degree. At a partial pressure of one atmosphere of hydrogen, therefore, $E = 0.3985 + 0.0004 = 0.3989$ volt. All these values were presumably obtained in terms of the old value of the standard Weston cell 1.0187 or 1.0186 at 20°. Using the new value 1.0183 lowers the value of E to 0.3988.

The recent value of Sebastian is 0.3990, and we shall accept this as the final value.

If we make the assumption, as before, that the actual potential of the calomel electrode is the same in 0.1M HCl and 0.1M KCl, then the same value of E holds for the combination[1]

$$\text{H}_2, \text{ HCl } (0.1M) \parallel \text{KCl } (0.1M), \text{HgCl, Hg;} \quad E = 0.3990. \quad (10)$$
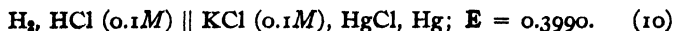
Numerous investigations in this laboratory have fixed the value of the e. m. f. between the decinormal and normal calomel electrode at 25° as —0.0530 volt. This includes the liquid potential between 0.1M KCl and 1M KCl, which cannot readily be calculated, owing to the change in the transference number of KCl with the concentration, and also to the fact that we have at present no method of applying the laws of dilute solution to a solution of KCl as concentrated as molal. In most exact e. m. f. measurements where the normal electrode has been used, 0.1 M KCl has been introduced between the normal electrode and the other electrode, so that it is really not important to know the value of the liquid potential in question, since we may regard the whole combination Hg, HgCl, KCl (1M), KCl (0.1M) as the normal electrode. We shall hereafter call this the normal electrode and designate it by N.E., thus

$$\text{Hg, HgCl, KCl } (0.1M), \text{ N.E.;} \quad E = -0.0530 \quad (11)$$

Adding (10) and (11) gives

$$\text{H}_2, \text{ HCl } (0.1M) \parallel \text{N.E.;} \quad E = 0.3460. \quad (12)$$

At the time of writing the preceding sections it was believed that the normal electrode potential of hydrogen could be calculated from the potential in 0.1M HCl with the desired accuracy, but the investigation of Lewis,[2] concerning the activity of univalent ions, showed that even in solutions as dilute as 0.1M the ion activity is in doubt by several per cent. For this reason, it seemed desirable to determine the hydrogen potential against more dilute solutions. This investigation, to which we have already referred, has been carried on by Mr. Sebastian, who has found for the cell

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[1] The two vertical bars indicate here, and elsewhere, that the value given is exclusive of the liquid potential at the junction indicated.

[2] Lewis, THIS JOURNAL, 34, 1631 (1912).

$$H_2, HCl\ (0.01M),\ KCl\ (0.01M),\ KCl\ (0.1M),\ N.E.;\ E = 0.4261.\quad(13)$$

Eliminating the liquid potentials[1]

$$HCl\ (0.01M),\ KCl\ (0.01M);\ E = 0.0274 \quad(14)$$

and

$$KCl\ (0.01M),\ KCl\ (0.1M);\ E = 0.0007 \quad(15)$$

we find

$$H_2, HCl\ (0.01M)\ \|\ N.E.;\ E = 0.3980 \quad(16)$$

According to the calculations of Lewis[2] the corrected degree of dissociation of $0.01M$ HCl would be the same as for $0.01M$ KCl, namely, 0.92 (which is 2% less than Λ/Λ_0 for $0.01M$ KCl).

We are now able to calculate the difference between the hydrogen electrode potential in $0.01M$ HCl and in hypothetical molal H^+. From the formula

$$E = 0.05915 \log (1/0.0092) = 0.1204$$

we find

$$H_2, HCl\ (0.01M)\ \|\ H^+\ (M),\ H_2;\ E = 0.1204 \quad(17)$$

and combining with (16) gives

$$N.E.\ \|\ H^+\ (M),\ H_2;\ E = -0.2776. \quad(18)$$

Since the normal hydrogen electrode is the standard *the potential of the normal calomel electrode is* $-0.2776\ v.$

Effect of Pressure and Temperature on the Hydrogen Electrode Potential.— In order to make sure that the hydrogen electrode actually operates in a reversible manner it is important to test the effect of both temperature and pressure upon the electromotive force. We have given above the equation for the effect of a change of the partial pressure of the hydrogen on its electrode potential. This effect was studied experimentally by Lewis, who raised the hydrogen pressure by allowing the gas which passed through the cell to escape through a column of water of varying height. The results are given in Table I, in which the absolute magnitude of the electromotive force has no significance but only its variation with the pressure.[3] The first line gives the excess pressure in centimeters of water, the second the measured electromotive force, the third the calculated electromotive force, using the first measurement as a basis.[4] The observed and calculated values agree to about $0.00001\ v.$

[1] We have assumed here and in the previous calculation the conductance values given by Bray and Hunt (THIS JOURNAL, **33**, 781 (1911)), for HCl, $\Lambda(0.1M) = 390.4$, $\Lambda(0.01M) = 411.6$; for KCl, $\Lambda(0.1M) = 129.0$, $\Lambda(0.01M) = 141.4$. The average transference number of K^+ in KCl between $0.1M$ and $0.01M$ has been taken as 0.494.

[2] Lewis, THIS JOURNAL, **34**, 1631 (1912).

[3] This cell was of the same type as those previously discussed but with a somewhat different hydrochloric acid concentration.

[4] This series of experiments occupied four hours. In the last experiment the pressure was released too suddenly, driving the liquid in the cell below the electrode,

Hg, HgCl, KCl (0.1M), N.E.; dE/dT = —0.00021   (21)
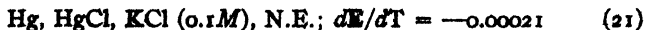
Combining (19), (20) and (21) gives

H$_2$, HCl (0.1M) || N.E.; dE/dT = 0.00167 — 0.0000580T. (22)
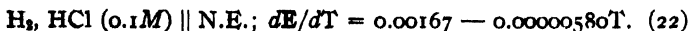
From equations (12) and (18) we find

H$_2$, HCl (0.1M) || H$^+$ (M), H$_2$; **E** = 0.0684.   (23)
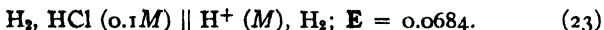
We may assume without serious error that the electromotive force of this cell is proportional to the absolute temperature. Therefore,

H$_2$, HCl (0.1M) || H$^+$ (M), H$_2$; dE/dT = 0.00023.   (24)

Combining (22) and (24) gives

N.E. || H$^+$ (M), H$_2$; dE/dT = —0.00144 + 0.0000580T. (25)

This is the temperature coefficient of the potential of the normal calomel electrode, since the potential of the normal hydrogen electrode is zero at all temperatures. It is very desirable that this important temperature coefficient be further investigated.

Hydroxide Ion.

The determination of the free energy of formation of hydroxide ion is involved with the determination of the free energy of formation of water and the free energy of ionization of water. We shall consider the latter process first.

H_2O (l) = H^+ + OH^-.—The difference between the potential of hydrogen in acid and alkaline solutions gives the most accurate means of determining the ionization constant of water. Accurate measurements of such cells have been made by Lorenz and Böhi[1] and by Lewis.[2] Lewis measured the cell: H$_2$, KOH (0.1M), KCl (0.1M), HgCl, Hg, and found **E** = 1.0836 at 25°, and **E** = 1.0799 at 18°. Corrected to the new value of the International Volt these values become **E** = 1.0833 at 25° and **E** = 1.0796 at 18°. The liquid potential KOH (0.1M), KCl (0.1M), calculated by the formula of Lewis and Sargent,[3] is 0.0165 at 25° and 0.0161 at 18°. Hence we find

H$_2$, KOH (0.1M) || (KCl (0.1M), HgCl, Hg;

E = 1.0998 (25°), 1.0957 (18°). (26) .

We have previously found

H$_2$, HCl (0.1M) || KCl (0.1M), HgCl, Hg;

E = 0.3990 (25°); 0.3978 (18°)   (27)
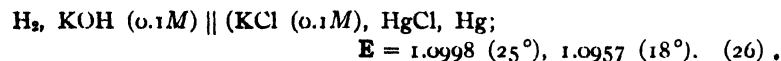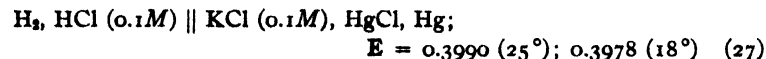
the value at 18° being obtained from the temperature coefficient given. Hence

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[1] Lorenz and Böhi, *Z. physik. Chem.*, **66**, 733 (1909).

[2] This is the same unpublished investigation which has been previously referred to

[3] We have used at 25° for KCl, as before, Λ (0.1M) = 129 0, Λ (0.01M) = 141 4; for KOH some preliminary measurements give Λ (0.1M) = 245, Λ (0.01M) = 256; at 18° for KCl Λ (0.1M) = 112.0, for KOH Λ (0.1M) = 213 (Kohlrausch).

H_2, KOH (0 1M) || HCl (0 1M), H_2,

$$E = 0\ 7008\ (25°),\ 0\ 6979\ (18°),\quad (28)$$
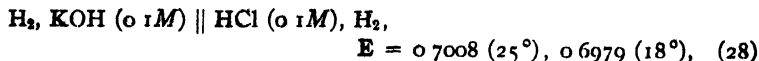
Lorenz and Bohi measured directly at several temperatures the cell

H_4, KOH (0 1M), KCl (0 1M), HCl (0 1M), H_2

$$E = 0\ 6560\ (25°),\ 0\ 6531\ (18°)\quad (29)$$

Excluding liquid potentials ($-0\ 0284$ and $-0\ 0165$ at 25°, and $-0\ 0286$ and $-0\ 0161$ at 18°) we find for (28) $E = 0\ 7009\ (25°)\ 0\ 6978\ (18°)$ The agreement between these values and those obtained by Lewis is surprisingly good [1] The former should, perhaps, be reduced one- or two tenths of a millivolt, owing to the change in the International Volt We may take the mean as 0 7008 at 25°, and 0 6978 at 18°

The recent measurements of Sebastian give at 25°

$$H_2,\ KOH\ (0\ 1M),\ KCl\ (0\ 1M),\ N\ E\quad E = 1\ 0303\quad (30)$$

$$H_2,\ KOH\ (0\ 01M),\ KCl\ (0\ 01M),\ KCl\ (0\ 1M),\ N\ E\ ,\ E = 0\ 9761\quad (31)$$

The liquid potentials are $-0\ 0165$ in the first cell, and $-0\ 0152$ and $0\ 0007$ (Equation 15) in the second cell Hence

$$H_2,\ KOH\ (0\ 1M)\ ||\ N\ E\ ,\ E = 1\ 0468\quad (32)$$

$$H\ ,\ KOH\ (0\ 01M)\ ||\ N\ E\ ,\ E = 0\ 9906\quad (33)$$

Combining these equations respectively with (12) and (16)

$$H_2,\ KOH\ (0\ 1M)\ ||\ HCl\ (0\ 1M),\ H_2,\ E = 0\ 7008\quad (34)$$

$$H_2,\ KOH\ (0\ 01M)\ ||\ HCl\ (0\ 01M),\ H_2\quad E = 0\ 5926\quad (35)$$

The value at 0 1M is identical with the result obtained above from the work of Lorenz and Bohi, and of Lewis It is to be noted that, if there is any error in the value of the liquid potential between KOH and KCl, it affects equally the results of the several observers

From (35) we are now in a position to calculate the ionization constant of water for $E = 0\ 5926 = 0\ 05915\ \log\ (a_1\ /a_2)$, where a_1/a_2 is the ratio of the activity or of the corrected concentration of H^+ in 0 01M HCl and in 0 01M KOH Hence $a_1\ /a_2 = 1\ 043 \times 10^{10}$ Now we will take as before the corrected concentration of H^+ in 0 01M HCl as 0 0092 and take the same value for the corrected concentration of OH^- in 0 01M KOH The ionization constant of water $(H^+)(OH^-)$ we may call K_w, hence

$$\frac{K_w}{0\ 0092} = \frac{0\ 0092}{1\ 043 \times 10^{10}}$$

whence $K_w = 0\ 81 \times 10^{-14}$ at 25°

This result is probably correct within 2%, the chief source of error entering in the estimation of the corrected degree of ionization of 0 01M KOH

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[1] It is perhaps worth while to point out that the values of Lorenz and Bohi and of Lewis were entirely independent the latter although unpublished were presented at the Baltimore meeting of the American Chemical Society in 1908 Those of Lorenz and Bohi were published in 1909

and HCl. The final value obtained by Heydweiller[1] from the conductivity of the purest water obtainable was 1.04×10^{-14}. All other methods which have been used for determining this important quantity have been subject to errors of at least 15 or 20%, owing to methods of calculation alone.

For the ionization of water we have from the measurements of Thomsen at 18°, $\Delta H = 13730$ and $\Delta \Gamma$ is about -44, whence $\Delta H_0 = 26540$ and

$$H_2O(l) = H^+ + OH^-; \Delta F^\circ_{298} = -R''T \ln K_w = 19235,[2] \quad (36)$$

$$\Delta F^\circ = 26540 + 44T \ln T - 275.19T. \quad (37)$$

This equation gives $K_w = 0.466 \times 10^{-14}$ at 18°, and 0.093×10^{-14} at 0°.

$1/2O_2 + 1/2H_2 + \ominus = OH^-$.—In order to obtain the free energy of this reaction it is necessary to know the free energy of formation of liquid water from its elements. In making this series of calculations we have attempted to avoid reference forward, but in this case we shall assume the equation (53) which will be obtained in a later section of this paper, namely,

$$H_2 + 1/2O_2 = H_2O(l); \Delta F^\circ_{298} = -56620.$$

Now combining this equation with (8) and (36) gives

$$1/2O_2 + 1/2H_2 + \ominus = OH^-, \Delta F^\circ_{298} = -37385. \quad (38)$$

$1/4O_2 + 1/2H_2O + \ominus = OH^-$.—The free energy of this reaction gives us the normal potential of the oxygen electrode. From (37) and (38)

$$\Delta F^\circ_{298} = -9075; E^\circ_{298} = -0.3933 \text{ v.}[3] \quad (39)$$

Water.

$H_2 + 1/2O_2 = H_2O$ (gas).—The existing data on the heat of formation of liquid water have been summarized by Lewis[4] and shown to be very concordant. The mean value is 68470 at 0°. The heat of vaporization of water at 100° has recently been the subject of careful research. Richards and Matthews[5] obtained the value 538.1 cals. per gram of water. A. W. Smith[6] has reviewed his earlier work upon this subject with extraordinary care and finds the value 540.7 cals. We will adopt the value 540.0 or 9730 cals. per mol. Taking 8.4 and 18.0 as the average molal heat ca-

[1] Heydweiller, *Ann. Physik*, **28**, 503 (1909).

[2] The absolute temperature corresponding to 25° is not 298 but approximately 298.1. Wherever the experimental data are sufficiently accurate to warrant the distinction ΔF_{298} will mean the free energy change at 25° = 298.1A

[3] It may be well to recall here the convention regarding the sign of **E**. The general equation is $\Delta F = -nEF'$ where n is the number of equivalents of positive electricity appearing on the left side of the chemical equation   In the present case, therefore, $n = -1$.

[4] Lewis, THIS JOURNAL, **28**, 1390 (1906).

[5] Richards and Matthews, *Proc. Amer. Acad.*, **46**, 511 (1911).

[6] A. W. Smith, *Phys. Rev.*, **34**, 173 (1911).

pacities of water vapor and liquid water between $0°$ and $100°$, the heat of vaporization at $0°$ becomes 10690   Combining this with the heat of formation of liquid water we find for the heat content of water vapor, $H_{273} = -57780$ cals   We have for the heat capacities of the other gases

$$H_2O, \ C_p = 8 81 - 0 0019 T + 0 00000222 T^2$$

$$H_2, \ C_p = 6 5 + 0 0009 T$$

$$1/ O_2, \ C_p = 3 25 + 0 0005 T$$

hence

$$\Delta P = 0 94 \quad 0 0033 T + 0 00000222 T \qquad (40)$$

and

$$\Delta H = \Delta H_0 - 0 94 T \quad 0 00165 T^2 + 0 00000074 T^3 \qquad (41)$$

Substituting the above value for ΔH_7 in this equation,

$$\Delta H_0 = 57410 \text{ cals},$$

and our free energy equation is

$$\Delta F° = 57410 + 0 94 T \ln T + 0 00165 T \quad 0 00000037 T^3 + IT \qquad (42)$$

For determining the value of I in the above equation several direct determinations of the dissociation of water vapor at high temperatures are available   Nernst and von Wartenberg[1] were the first to investigate this important equilibrium, and later measurements by different methods were made by Lowenstein,[2] von Wartenberg[3] and Langmuir[4]   The measurements of Holt[5] were obviously lacking in self-consistency and can be given no weight[6]   The results obtained by these investigators are given in Table III   The first column indicates the names of the in vestigators, the second the absolute temperature, the third the measured percentage dissociation, and the fourth the equilibrium constant $K_p = [H_2O]/[H_2][O_2]^{1/2}$, where the brackets indicate the pressure of the gases in question

From each of these values of K_p we may determine a value for I Thus, the measurements of Nernst and von Wartenberg give $I = 3 81, 3 91, 3 67$, respectively, average 3 81   Langmuir's values lead to the average value $I = 3 55$, with about the same mean deviation   Lowenstein's results show greater variation and lead to the average value $I = 3 71$, while von Wartenberg's two measurements at the highest temperatures

[1] Nernst and von Wartenberg, *Z physik Chem* **54**, 715 (1905)

[2] Löwenstein, *Ibid*, **54**, 715 (1905)

[3] von Wartenburg, *Ibid*, **56**, 513 (1906)

[4] Langmuir, THIS JOURNAL, **28**, 1357 (1906)

[5] Holt, *Phil Mag*, [6] **13**, 630 (1907)

[6] In a case of this kind where a large number of data for a given equilibrium at different temperatures are available, a very good idea of the consistency of the various determinations may be obtained by plotting log K_p against $1/T$

TABLE III.

	T	Per cent. dissoc.	K_p	Log K_p
Nernst and von Wartenberg	1397	0 0078	2 05 × 10⁶	6 312
	1480	0 0184	5.66 × 10⁵	5 753
	1561	0 0340	2 26 × 10⁵	5 354
Löwenstein	1705	0 0326	2 3 × 10⁴	4 362
	1783	0 0778	1 82 × 10⁴	4 260
	1863	0 211	6 70 × 10³	3 826
	1968	0 373	3 79 × 10¹	3 579
von Wartenberg	2155	1 18	1 094 × 10²	3 039
	2257	1 77	0 590 × 10¹	2 771
Langmuir	1325	0 00325	7 65 × 10⁶	6.884
	1354	0 0049	4 13 × 10⁶	6 616
	1393	0 0069	2 47 × 10⁶	6 393
	1433	0 0103	1 35 × 10⁶	6 129
	1455	0 0142	8 35 × 10⁵	5 922
	1474	0 0141	8 45 × 10⁵	5 927
	1531	0.0255	3 47 × 10⁵	5 540
	1550	0 0287	2 91 × 10⁵	5 464

give 3.67 and 3.57, average 3.62. We may take as the weighted mean[1] of all these results I = 3.66. Substituting this value of I in our equation we find

$$\Delta F^\circ_{298} = -54590 \qquad (43)$$

We shall not, however, regard these values of ΔF°_{298} and of I as final, since there are other important methods of determining the free energy of formation of water still to be considered.

$H_2O(g) = H_2O(l)$.—The free energy of formation of liquid water from gaseous water may be obtained from the vapor pressure. According to Scheel and Heuse[2] the vapor pressure of water at 25° is 23.8/760 atms. Assuming that water vapor at this temperature and pressure is sufficiently near to a perfect gas,

$$\Delta F^\circ_{298} = -R'T \ln \frac{760}{23.8} = -2053 \qquad (44)$$

$H_2 + {}^1/_2 O_2 = H_2O(l)$.—Combining (43) and (44) gives

$$\Delta F^\circ_{298} = -56640 \text{ cals.}$$

We shall not accept this as the final value but proceed to the discussion of the other methods of determining this quantity.

[1] We have not included in this calculation measurements of the electromotive force of the oxygen, hydrogen, water vapor cell by Haber and his students. These experiments, although not capable of being carried out with the same accuracy as the equilibrium measurements, furnish a further important check upon the correctness of the results obtained by the latter methods.

[2] Scheel and Heuse, *Ann. Physik*, [4] 31, 715 (1910). See also the very recent determination of Derby, Daniels and Gutsche, THIS JOURNAL, 36, 793 (1914).

The Free Energy of Water from the Dissociation of Silver Oxide —From measurements at higher temperatures, Lewis[1] calculated the decomposition pressure of silver oxide at $25°$ to be 5×10^{-4}, whence we calculate

$$2Ag + {}^1/_2O_2 = Ag_2O, \quad \Delta F°_{298} = -2250 \qquad (45)$$
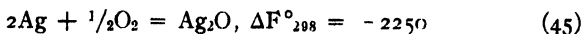
According to the measurements of Bottger, silver oxide is in equilibrium with water containing Ag^+ and OH at $1 4 \times 10^{-4} M$[2] Assuming that, at this concentration, the activity of the ions is proportional to their concentration,

$$Ag_2O + H_2O = 2Ag^+ + 2OH^- \quad \Delta F°_{298} = 21040 \qquad (46)$$
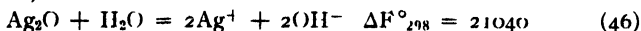
Finally we need for this calculation the free energy of formation of Ag^+ The cell Ag, $AgNO_3$, (o 1M), KNO_3 (o 1M), KCl (o 1M), HgCl, Hg was investigated by Lewis[3] who found $E_{298} = -0 399$ Noyes and Brann[4] have studied this same cell more recently and find $E = -0 3992$ Eliminating the liquid potentials ($-0 0025$, $+0 0018$) and referring to the normal electrode by (11)

$$Ag, AgNO_3 \text{ (o 1}M) \parallel N E , \quad E = -0 4515 \qquad (47)$$
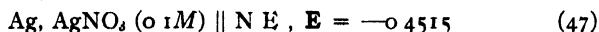
There is no way of calculating directly from existing data the activity or the corrected concentration of o 1M $AgNO_3$ But, if we assume that the properties of silver nitrate are approximately the same as those of the analogous thallous nitrate, we may estimate this quantity Noyes[5] found that the lowering of the solubility of TlCl by KCl (o 1M) and TlNO₃ (o 1M) indicated a concentration of Tl^+ 10% less than the concentration of K^+ Lewis[6] showed by a combination of conductivity and transference data the degree of dissociation of $TlNO_3$ and $AgNO_3$ to be 8% less than that of KCl at this concentration Taking the corrected concentration of K^+ in KCl (o 1M) as o 074 we will therefore, conclude that that of Ag^+ in $AgNO_3$ (o 1M) is o 067 Hence

$$Ag, Ag^+ (M) \parallel AgNO_3 \text{ (o 1}M) Ag, \quad E = -0 0694 \qquad (48)$$
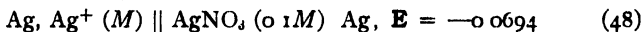
From (47), (48) and (18) we therefore find for the potential of silver against (hypothetical) molal silver ion

$$Ag, Ag^+ (M) \parallel H^+ (M), H_2, \quad E°_{298} = -0 7985 \qquad (49)$$

and

$$Ag + H^+ = {}^1/_2H_2 + Ag^+, \quad \Delta F°_{298} = 18424 \qquad (50)$$
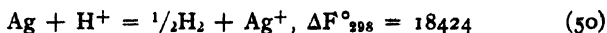
We may now combine[7] (45), (46), (50) and (36), namely,

[1] Lewis THIS JOURNAL **28,** 139 (1906)

[2] Lewis, The Potential of the Oxygen Electrode, *Ibid* **28,** 164 (1906)

[3] Lewis *Ibid* **28,** 107 (1906)

[4] Noyes and Brann, *Ibid* **34,** 1026 (1912)

[5] Noyes *Z physik Chem* **9,** 603 (1892)

[6] Lewis THIS JOURNAL **34,** 1641 (1912)

[7] The last three of the four equations used above may be combined to give the equation $Ag_2O + H_2 = H_2O + 2Ag$ In place of the laborious and perhaps somewhat doubtful calculations used in these three reactions, a determination of the e m f of

$$2Ag + \tfrac{1}{2}O_2 = Ag_2O; \qquad \Delta F°_{298} = -2250$$
$$Ag_2O + H_2O = 2Ag^+ + 2OH^-; \qquad \Delta F°_{298} = 21040$$
$$2Ag^+ + H_2 = 2H^+ + 2Ag; \qquad \Delta F°_{298} = -36848$$
$$2OH^- + 2H^+ = 2H_2O; \qquad \Delta F°_{298} = -38470.$$

Adding we find
$$H_2 + \tfrac{1}{2}O_2 = H_2O(l); \quad \Delta F°_{298} = -56530.$$
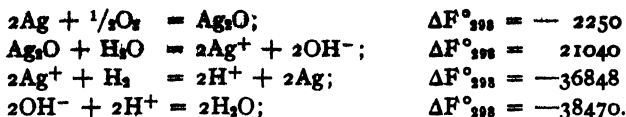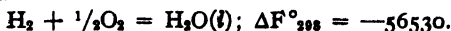
The Free Energy of Formation of Water from the Dissociation of Mercuric Oxide.—Another similar calculation has been made by Brönsted[1] from the dissociation pressure of mercuric oxide, measured by Pélabon, and from his own measurements of the e. m. f. of the cell, H_2, NaOH (aq), HgO, Hg, which is independent of the concentration of NaOH, provided that this is not great enough to lower materially the activity of the water in which it is dissolved. Brönsted found for this cell (H_2 at one atmosphere), $E_{298} = 0.9268$, hence,

$$H_2 + HgO = H_2O(l) + Hg(l); \quad \Delta F°_{298} = -42770. \qquad (51)$$
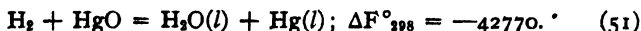
Taylor and Hulett[2] have just redetermined the dissociation pressure of HgO. From their measurements it appears that at the boiling point of mercury, $357°$, the oxide is in equilibrium with the gas which it produces, when the total pressure is 86 mm. Now one-third of this gas is oxygen and two-thirds mercury. Reducing pressures to atmospheres we find $K = [Hg][O_2]^{1/2} = 0.0146$. At this temperature liquid mercury is in equilibrium with its vapor at 1 atm., therefore, $\Delta F°_{630} = -R'T \ln K = 5290$ is also the free energy change for the reaction $HgO = Hg(l) + \tfrac{1}{2}O_2$.

The heat of this reaction was found by Varet[3] as $-21,500$ and by Brönsted as -21700 cals. We may take the average $\Delta H = 21600$. The change in heat capacity in this reaction is zero, within the limits of accuracy of existing data, and $\Delta F° = 21600 + IT$, hence, from the above value of $\Delta F°_{630}$, $I = -25.9$ and

$$HgO = Hg(l) + \tfrac{1}{2}O_2; \quad \Delta F°_{298} = 13880. \qquad (52)$$

Combining (51) and (52) gives
$$H_2 + \tfrac{1}{2}O_2 = H_2O(l); \quad \Delta F°_{298} = -56650.$$
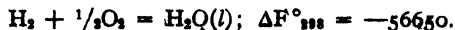
Final Value for the Free Energy of Water and the Electromotive Force of the Hydrogen Oxygen Cell.—We have found above three independent and extraordinarily concordant values for the free energy of formation of liquid water at $25°$, namely, -56640, from the measurements of Nernst the cell Ag, Ag_2O, NaOH, H_2 should give the desired result. Luther and Pokorny' (*Z. anorg Chem*, 57, 290 (1908)) have measured this cell at $25°$ and found $E = 1.172$. This would give for the free energy of liquid water -56335. Their measurements, however, were only certain to within a few millivolts and we shall prefer for the present the calculations which we have used above.

[1] Brönsted, *Z. physik. Chem.*, 65, 84 and 744 (1909).
[2] Taylor and Hulett, *J. Phys. Chem.*, 17, 565 (1913).
[3] Varet, *Ann. chim. phys.*, [7] 8, 100 (1896).

and von Wartenberg, of Löwenstein, and of Langmuir; —56530 from the measurements of Lewis; —56650 from the measurements of Brönsted and of Taylor and Hulett. These values correspond to 1.2275, 1.2250, and 1.2276 volts for the electromotive force of the hydrogen-oxygen cell. We may take, as a kind of *weighted mean*, *1.2270 v.* The corresponding *average of the free energy values is*

$$H_2 + \frac{1}{2}O_2 = H_2O(l); \quad \Delta F°_{298} = -56620. \tag{53}$$
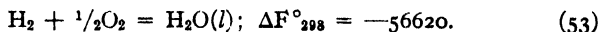
The heat capacity of water is not constant, nor can it be expressed as a linear function of the temperature. However, over the range from 0° to 300°, which alone is of practical importance, we may, with sufficient accuracy, regard the value of $\Delta\Gamma$ as constant and equal to 8.0. We have seen that for this reaction $\Delta H_{273} = -68470$, whence,

$$\Delta F° = -70650 - 8.0T \ln T + 92.64T. \tag{54}$$

Combining (44) and (53) gives

$$H_2 + \frac{1}{2}O_2 = H_2O(g); \quad \Delta F°_{298} = -54567, \tag{55}$$

and redetermining the value of I for this reaction in (42) we find

$$\Delta F° = -57410 + 0.94T \ln T + 0.00165T^2 - 0.00000037T^3 + 3.72T. \tag{56}$$

$H_2O(s) = H_2O(l)$.—Instead of determining the general equation for the free energy of formation of ice it will be more convenient to obtain a simpler equation for the free energy of fusion of ice, valid over a small range of temperature. The best value for the heat of fusion is 79.7 cals. per gram, or 1436 cals. per mol.[1] The difference between the heat capacities of water and ice is neither constant nor accurately known. In the neighborhood of the freezing point we may take this difference as 9.0, and since the free energy of fusion is zero at 0°, we find[2]

$$H_2O(s) = H_2O(l); \quad \Delta F°_{298} = -141.6$$
$$\Delta F° = -1022 - 9.0T \ln T + 54.230T. \tag{57}$$

$H_2 + \frac{1}{2}O_2 = H_2O(s)$.—Combining with (53) gives $\Delta F°_{298} = -56478$.

[1] A. W. Smith, *Phys. Rev.*, **17**, 193 (1903); Roth, *Z. physik. Chem.*, **63**, 442 (1908). It is interesting to note that the value now accepted for the heat of fusion of ice is identical with the value 79.7 obtained by Black in 1762

[2] In order to use such an equation as (57) over a small range from a melting point or a transition point with the accuracy justified by experiments, it is necessary to use 7 or 8-place logarithm tables in many cases. In order to avoid this we may substitute in such an equation as (57), $\Theta + t$ for T, where t is the temperature above the transition temperature Θ. Expanding the various terms and neglecting all terms of higher order than t^3 gives

$$\Delta F = -\frac{\Delta H_0}{\Theta}t - \frac{\Delta\Gamma}{2\Theta}t^2 + \frac{\Delta\Gamma}{6\Theta^2}t^3. \tag{58}$$

In this particular case Θ is 273.1° and t is the centigrade temperature. Substituting the numerical values,

$$\Delta F = -5.26t - 0.0165t^2 + 0.00002t^3. \tag{59}$$

This equation will be found especially useful in determining the free energy of solutions from freezing point data.

Hydrogen Peroxide.

The oxidizing potential of an oxygen electrode is diminished by the addition of hydrogen peroxide. Measurements[1] of such an electrode potential have been supposed to give material for the calculation of the free energy of hydrogen peroxide, but in this case, as in the case of ozone, there is no satisfactory evidence that the electromotive force is due to a single definite reversible reaction.

Traube[2] obtained a yield of 0.74% of H_2O_2 by directing an oxyhydrogen flame against water. The temperature of the flame was probably between 2000° and 3000°, but it is obviously impossible to obtain any quantitative estimate of the free energy of formation of hydrogen peroxide from this observation. We shall obtain a moderately accurate solution of this problem by considering the dissociation pressure of barium peroxide, and the equilibrium between barium peroxide hydrate and water.

$BaO + 1/2O_2 = BaO_2$.—According to Berthelot, $\Delta H_{291} = -17200$. The later measurements of de Forcrand[3] give $\Delta H = -18400$. We will use the value -18000. The change in heat capacity in this reaction is small and will be neglected. Hence

$$\Delta F° = -18000 + IT. \qquad (60)$$

We may calculate the value of I from the dissociation pressures given by Le Chatelier.[4] Except at the lower temperatures, his pressures lead to a constant value of I, namely, 16.8, whence $\Delta F°_{298} = -13000$.

Hildebrand[5] made a careful investigation of the dissociation of barium peroxide and found that the reaction did not occur except in the presence of water (and, therefore, barium hydroxide) as catalyzer. His results apparently indicated a considerable mutual solubility of BaO in BaO_2, but an inspection of his curves makes it seem equally probable that the $Ba(OH)_2$ was largely responsible for the phenomena which he attributed to solid solution, and that in his univariant system the BaO and BaO_2 behave as nearly pure substances. We shall, therefore, calculate I directly from Hildebrand's several oxygen pressures and obtain very constant results, average I = 16.1, whence we find as final value

$$BaO + 1/2O_2 = BaO_2; \; \Delta F°_{298} = -13200 \qquad (61)$$

$BaO_2.10H_2O = BaO_2 + 10H_2O(g)$.—In the presence of water at ordinary temperatures, BaO_2 forms a hydrate, which, according to the work of de Forcrand,[6] is $BaO_2.10H_2O$. In order to complete the necessary free energy

[1] Haber and Grinberg, Z. anorg. Chem., **18**, 37 (1898); Haber, Z. Elektrochem., **7**, 441, 1043 (1901); Nernst, Z. physik. Chem., **46**, 720 (1903).

[2] Traube, Ber., **18**, 1890 (1885).

[3] de Forcrand, Ann. chim. phys., [8] **15**, 433 (1908).

[4] Le Chatelier, Compt. rend., **115**, 654 (1892)

[5] Hildebrand, This Journal, **34**, 246 (1912)

[6] de Forcrand, Compt. rend., **130**, 778, 834 (1900).

equations we have, therefore, measured the pressure of water vapor over a mixture of BaO_2 and $BaO_2.10H_2O$. The measurements were made with a differential mercury manometer so arranged that either limb could be exhausted at will. The vapor pressure proved to be only slightly less than that of pure water. The mean results of several determinations were 15 mm. at 22°, 18.6 mm. at 25°, 28.3 mm. at 31°. Hence

$$\Delta F°_{298} = 22000.$$

H_2O_2 (aq) $= H^+ + HO_2^-$.—Hydrogen peroxide in aqueous solution is a weak acid. Joyner[1] found its ionization constant to be $K = 0.67 \times 10^{-12}$ at 0°, and $K = 2.4 \times 10^{-12}$ at 25°. Hence

$$\Delta F°_{273} = 15,220; \quad \Delta F°_{298} = 15860. \tag{63}$$

H_2O_2 (aq) $+ OH^- = HO_2^- + H_2O$.—When hydrogen peroxide combines with an alkali it is merely a matter of preference whether we regard H_2O_2 as an acid forming a salt with the alkali, or consider that the H_2O_2 forms a complex with OH^- according to the reaction $OH^- + H_2O_2 = H_3O_3^-$. This last ion differs only in hydration from HO_2^-, and the equation may equally well be written as above. The equilibrium constant of this reaction $(HO_2^-)/(OH^-)(H_2O_2)$ is obtained by dividing the above values of K by K_w obtained from (36). Hence

$$K_{273} = 720, \quad K_{298} = 300.$$

$BaO_2.10H_2O = Ba^{++} + 2OH^- + H_2O_2$ (aq) $+ 8H_2O$.—We have attempted to determine the equilibrium corresponding to this reaction, when the hydrated barium peroxide is shaken up with water. Unfortunately the solution of the peroxide hydrate, notwithstanding the large surface exposed, is very slow, and the rate of decomposition of hydrogen peroxide in alkaline solution is appreciable. In order to obviate these difficulties as far as possible, the mixture was vigorously stirred in a bath at 0°. The analysis of the resulting solutions is given in Table IV (Experiments 8 and 9). The equilibrium was also approached from the other side. Solutions of $Ba(OH)_2$ and H_2O_2 were mixed and stirred in the absence of

TABLE IV.

		Time Hours	$Ba(OH)_2$ Millimols per l	H_2O_2 Millimols per l
1	.	5	2 68	5 44
2	.	8	2 74	5 36
3	.	6	2 78	2 06
4		5	107 0	<0 05
5	.	7	2 66	5 36
6		7	3 29	12 50
7		6	2 98	8 60
8		6	2 87	1 56
9	.	. .	24	6 38	0 20

[1] Joyner, Z anorg Chem, **77**, 103 (1912)

carbon dioxide and the resulting solutions were filtered by forcing the solution through an asbestos filter, and analyzed (Experiments 1–7). Table IV gives the results of the analyses.

At the time when these measurements were made it was not possible to interpret them, but the recent determination by Joyner of the ionization constant of H_2O_2, to which we have already referred, enables us to calculate the concentrations of the various constituents of the solution which we analyzed. We have seen in a previous section that at 0°, $(HO_2^-)/(H_2O_2)(OH^-) = 720$. Assuming that the activity of the ions in these pretty dilute solutions is proportional to the concentrations as ordinarily determined by conductance measurements, and taking the degree of ionization of $Ba(OH)_2$ and of $Ba(HO_2)_2$ as 0.86 when the barium concentration is 0.06M, and 0.90 at 0.0027M, and solving by a series of approximations,[1] we find the concentrations in millimols per liter of the various constituents as given in Table V.

TABLE V

	(Ba^{++})	(HO_2^-)	(OH^-)	(H_2O_2)	$K \times 10^{13}$
1	2 41	2 94	1 88	2 17	18 5
2	2 47	2 96	1 97	2 07	19 8
3	2 50	1 38	3 62	0 52	17 1
5	2 40	2 90	1 89	2 14	18 4
6	2 95	4 93	0 97	7 02	19 5
7	2 68	4 01	1 35	4 15	20 3
8	2 58	1 08	4 08	0 36	15 5
9	5 50	0 15	10 80	0 02	13 0

The equilibrium constant $K = (Ba^{++})(OH^-)^2(H_2O_2)$ is given in the last column. The constancy of this product is far better than could have been anticipated. The calculation is necessarily such as to magnify greatly the experimental errors, and this is especially true in Experiments 3, 8, and 9, where the H_2O_2 was nearly all combined. Excluding these three measurements the average is $K_{273} = 19.3 \times 10^{-13}$.

From the thermochemical investigations of de Forcrand, we find for the above reaction $\Delta H = 23700$, and applying the Van't Hoff equation $K_{298} = 7.48 \times 10^{-10}$, whence

$BaO_2.10H_2O = Ba^{++} + OH^- +$
$$H_2O_2(aq) + 8H_2O; \Delta F°_{298} = 12450. \quad (64)$$
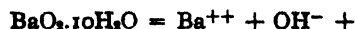
$BaO + H_2O(l) = Ba^{++} + 2OH^-$.—In order to determine the free energy of formation of hydrogen peroxide from the preceding equations it remains to determine the free energy of solution of barium oxide. An inspection of the literature seems to show the availability of two different

[1] The equations used in this calculation are $2(Ba^{++}) = (HO_2^-) + (OH^-)$, $\Sigma(H_2O_2) = (H_2O_2) + (HO_2^-)/\alpha$, where α is the degree of ionization of $Ba(OH)_2$ or $Ba(HO_2)_2$, and $(HO_2^-)/[(H_2O_2)(OH^-)] = 720$.

methods for making this calculation from existing data. First, we might combine the following equations:

$$BaO + CO_2 = BaCO_3 \qquad (a)$$
$$BaCO_3 = Ba^{++} + CO_3^{--} \qquad (b)$$
$$2H^+ + CO_3^{--} = H_2CO_3(aq) \qquad (c)$$
$$H_2CO_3(aq) = H_2O + CO_2 \qquad (d)$$
$$2H_2O = 2H^+ + 2OH^- \qquad (e)$$
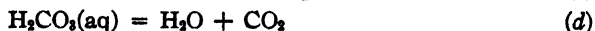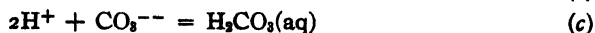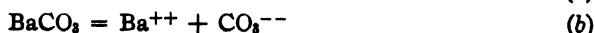
The free energy of reaction (a) at $25°$ has been calculated by Johnston[1] from the experiments of Finkelstein;[2] that of (b) may be obtained from the solubility of $BaCO_3$; (c) from the hydrolysis of Na_2CO_3 and $NaHCO_3$; (d) from the solubility of carbon dioxide; and (e) from results already obtained in this paper. Unfortunately we find by referring to the original paper of Finkelstein that his dissociation pressures are not obtained from a system containing the two solids, BaO and $BaCO_3$, but from one involving a liquid mixture of these two substances, and it is impossible from his data to determine the free energy of reaction (a).

The second method consists in the combination of the followinge quations:

$$Ba(OH)_2.8H_2O = Ba^{++} + 2OH^- + 8H_2O(l) \qquad (f)$$
$$Ba(OH)_2H_2O + 7H_2O(g) = Ba(OH)_2.8H_2O \qquad (g)$$
$$Ba(OH)_2 + H_2O(g) = Ba(OH)_2H_2O \qquad (h)$$
$$BaO + H_2O(g) = Ba(OH)_2 \qquad (i)$$
$$9H_2O(l) = 9H_2O(g) \qquad (j)$$
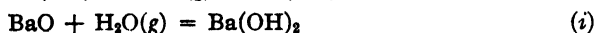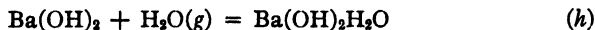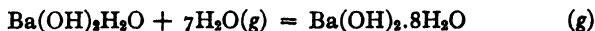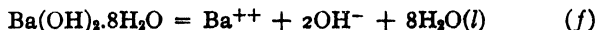
(f) The solubility of barium hydroxide octahydrate in water at $ρ°$ is almost exactly $0.1M$.[3] Now, from a consideration of the freezing-point lowering of several uni-bivalent salts, we find, by the method used by Lewis,[4] that the increase in free energy from a $0.1M$ solution to one in which each ion is in hypothetical molal concentration is about 3610 cals. This then is $\Delta F°_{273}$ for the above reaction. The heat of solution according to de Forcrand is -14500, whence $\Delta F°_{298} = 2610$.

(g) From the vapor pressures at different temperatures over a mixture of $Ba(OH)_2.8H_2O$ and $Ba(OH)_2H_2O$ measured by Lescoeur[5] we find the vapor pressure at $25°$ to be 9.1 mm., whence $\Delta F°_{298} = -18350$.

[1] Johnston, THIS JOURNAL, 30, 1357 (1908).

[2] Finkelstein, Ber., 39, 1585 (1906).

[3] Landolt-Börnstein-Roth; Tabellen.

[4] Lewis, THIS JOURNAL, 34, 1635 (1912). The change in free energy between $0.1M$ and $0.001M$ was first determined, namely, 6960. At $0.001M$ intermediate ions were assumed to be absent and the degree of dissociation, 0.96, was taken from conductivity data. The increase in free energy between $0.001M$ and a solution hypothetical molal with respect to each ion is then equal to $-R'T \ln 0.0096 \times (0.00192)^2 = 10570$. See also Lewis and Lacey, THIS JOURNAL, 36, 804 (1914).

[5] Lescoeur, Compt. rend., 103, 1260 (1887).

(*h*) Lescoeur found the vapor pressure over a mixture of $Ba(OH)_2H_2O$ and $Ba(OH)_2$ at $100°$ to be 45 mm. According to the work of de Forcrand the heat of this reaction is 14800, whence $p_{298} = 0.3$ mm., and $\Delta F°_{298} = -4650$.

(*i*) The thermal dissociation of barium hydroxide has been investigated by Johnston,[1] who calculated from his data the free energy of the reaction at $25°$. This calculation, however, was based on the assumption that the barium hydroxide was solid at the temperatures investigated. The melting point of barium hydroxide has apparently not been accurately determined, but several observers state that it melts at a dull red heat. We may assume, therefore, that the difference in free energy between liquid and solid $Ba(OH)_2$ is small at the lowest temperature investigated by Johnston, namely $647°$, at which temperature the pressure obtained from his curve is 12 mm. Assuming, further, that BaO at this temperature is not sufficiently soluble in $Ba(OH)_2$ to lower materially the activity of the latter, we find for reaction (*i*) $\Delta F°_{920} = -7590$. The heat of this reaction according to measurements of de Forcrand is 34700 and the change in heat capacity is very nearly zero. Hence $\Delta F°_{298} = -25900$.

(*j*) The free energy of this reaction from (44) is $\Delta F°_{298} = 18480$.

Adding reactions[2] (*f*)–(*j*),

$$BaO + H_2O(l) = Ba^{++} + 2OH^-, \quad \Delta F°_{298} = -27870 \qquad (65)$$

$H_2 + O_2 = H_2O_2$ (*aq*).—We are now in a position to calculate the free energy of formation of aqueous H_2O_2. Equations (61), (62), (64), (65), (53) and (44) give (all at $298°$ A)

$Ba + \frac{1}{2}O_2 = BaO_2$;	$\Delta F° = -13200$
$BaO_2 + 10H_2O(g) = BaO_2.10H_2O$;	$\Delta F° = -22000$
$BaO_2.10H_2O = Ba^{++} + 2OH^- + H_2O_2(aq) + 8H_2O(l)$;	$\Delta F° = 12450$
$Ba^{++} + 2OH^- = BaO + H_2O(l)$;	$\Delta F° = 27870$
$H_2 + \frac{1}{2}O_2 = H_2O(l)$;	$\Delta F° = -56620$
$10H_2O(l) = 10H_2O(g)$;	$\Delta F° = 20530$
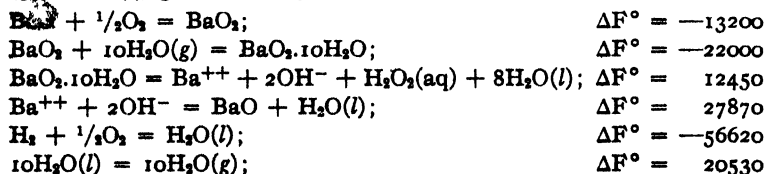
Adding all these equations as they stand gives the final result

$$H_2 + O_2 = H_2O_2 \text{ (aq)}; \quad \Delta F°_{298} = -30970. \qquad (66)$$
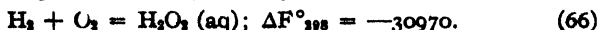
In this determination of the free energy of formation of molal aqueous H_2O_2 it is difficult to estimate the probable error. The chief source of error lies in the determination of the free energy of solution of barium oxide.

$\frac{1}{2}H_2 + O_2 + \ominus = HO_2^-$.—We may now obtain the free energy of formation of the hydroperoxide ion from (63), (66) and (9).

$$\Delta F°_{298} = -15110.$$

[1] Johnston, This Journal, 30, 1357 (1908).

[2] The corresponding value obtained by adding equations (*a*) to (*e*), on the assumption that the reaction measured by Finkelstein was that between solid BaO and solid $BaCO_3$ is $\Delta F° = -26730$. The difference is in the direction to be expected as a consequence of this false assumption.

$H_2O_2(aq) = H_2O(l) + 1/2O_2$.—This reaction is important because its free energy shows the tendency for aqueous hydrogen peroxide to decompose. Combining (66) and (53) gives

$$\Delta F^\circ_{298} = -25650. \tag{67}$$

Nernst, from e. m. f. measurements, obtained the value —17100, differing from the above by 8500 cals. It is extremely improbable that our value can be in error by one-tenth of this difference. This difference makes an enormous change in the calculation of the equilibrium constant in the vapor phase studied by Nernst, namely, $[H_2O_2]^2/[H_2O]^2[O_2]$. If our calculations are correct the value of Nernst for this constant is erroneous by a factor of 10^{12} as will be shown presently.

$H_2O_2(l) = H_2O_2(g)$.—The experiments of Wolffenstein[1] and of Brühl[2] show the vapor pressure of pure H_2O_2 to be 29 mm. at 69° and 65 mm. at 85°. Hence we find the heat of vaporization per mol to be 12300 cals.,[3] whence the vapor pressure at 25° is 2.1 mm. and

$$\Delta F^\circ_{298} = 3500. \tag{68}$$

$H_2O_2(aq) = H_2O_2(g)$.—If the law of perfect solutions were applicable to a mixture of H_2O and H_2O_2 the vapor pressure of H_2O_2 (M) would be $2.1/56.5 = 0.037$ mm. Some distillation experiments of Nernst[4] seem to indicate that the vapor pressure is, however, only about one-fourth or one-fifth of that corresponding to Raoult's law. We may take 0.01 mm. as a rough approximation, and

$$\Delta F^\circ_{298} = RT \ln (760/0.01) = 6700. \tag{69}$$

$H_2 + O_2 = H_2O_2(l)$.—Combining (66), (68) and (69),

$$\Delta F^\circ_{298} = -27770. \tag{70}$$

$H_2 + O_2 = H_2O_2(g)$.—Adding (66) and (69) gives

$$\Delta F^\circ_{298} = -24270. \tag{71}$$

The value of ΔH for this reaction may be found by combining the above heat of vaporization of H_2O_2 with the thermochemical data of Thomsen and de Forcrand, which gives $\Delta H_{291} = -32600$. The heat capacity of gaseous H_2O_2 has not been determined. We will assume that it is approximately the same as that of ammonia, the only tetratomic gas which has been investigated. Thus

$$H_2O_2; \; C_p = 7.5 + 0.0042T$$
$$H_2; \; C_p = 6.5 + 0.0009T$$

[1] Wolffenstein, *Ber.*, **27**, 3307 (1894).

[2] Brühl, *Ibid.*, **28**, 2847 (1895).

[3] From these data the boiling point of H_2O_2 is 144°, and the constant of Trouton's rule, $K = \Delta H/T$, is 29.5. This unusually high value was to be expected. Hydrogen peroxide must be a very abnormal liquid, as shown, for example, by the fact that it has the highest of all dielectric constants.

[4] Nernst, *Z. physik Chem.*, **46**, 720 (1903).

$$O_2; \quad C_p = 6.5 + 0.0010T$$
$$\Delta \Gamma = -5.5 + 0.0023T$$

and

$$\Delta F^\circ = -31100 + 5.5T \ln T - 0.00115T^2 - 8.08T \qquad (72)$$

where the value of I is obtained from the above value of ΔF°_{298}.

From this equation, it appears that hydrogen peroxide cannot be formed spontaneously in appreciable amount from oxygen and hydrogen except below 1000°.

$H_2O(g) + \frac{1}{2}O_2 = H_2O_2(g)$.—The general equation for the free energy of this reaction may be found by combining Equations (56) and (72).

$$\Delta F^\circ = 26310 + 4.56T \ln T - 0.0028T^2 + 0.00000037T^3 - 11.80T. \quad (73)$$

From this equation we calculate that the pressure of H_2O_2 in equilibrium with water vapor and oxygen, each at atmospheric pressure, is 1×10^{-7} atm. at 2000° A, and 3×10^{-6} atm. at 3000° A. The experiment of Traube, already referred to, in which a considerable yield of H_2O_2 is obtained by the rapid cooling of an oxyhydrogen flame cannot, therefore, be explained by assuming that H_2O_2 is largely present in the gases in the hottest portion of the oxyhydrogen flame. It must be explained rather by assuming that in the colder parts of the flame, probably between 500° and 1000° C., hydrogen and oxygen combine directly to form hydrogen peroxide.

In concluding, we wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

We shall not attempt to summarize further a paper which is itself a summary of numerous investigations, several of which have not hitherto been published. We have, however, collected in Table VI the values for the free energy of formation of eleven substances from the elements in their standard states. The table also shows the number of the equation connecting the free energy of formation and the temperature.

TABLE VI.

Substance.	F°_{298}	Equation	Substance	F°_{298}	Equation
O_2	32400	5	$H_2O(g)$	—54567	56
H	30550	7	$H_2O(s)$	—56478	
H^+	0	9	$H_2O_2(aq)$	—30970	
OH^-	—37385		HO_2^-	—15110	
$H_2O(l)$	—56620	54	$H_2O_2(l)$	—27770	
			$H_2O_2(g)$	—24270	

We also append to this paper a short table of numerical constants, which we have found extremely useful in these calculations, and which may be of use to others.

<div align="center">

TABLE VII.
</div>

		z.	Log z.
1 cc.-atms.	= x joules	0.10133	9.005737
1 cc.-atms.	= x cals.	0.02423	8.384353
1 cal. (15°)	= x joules	4.182	0.621384
Absolute zero	= $-x°$ C.	273.09	2.436306
Molal gas volume (0° C., 1 atms.)	= x cc.	22412	4.350481
R′	= x cals per degree	1.9885	0.298528
R	= x joules per degree	8.3160	0.919912
R″	= x cc.-atms. per degree	82.07	1.914175
F	= x coulombs per equiv.	96494	4.984500
F′	= x cals. per volt-equiv.	23074	4.363116
ln ( )	= x log ( )	2.3026	0.362216
R′ ln ( )	= x log ( )	4.5787	0.660744
(R/F) ln ( )	= x log ( )	0.00019844	6.297626
25° C.	= $x°$ A	298.1	2 474362
ln 298.1	= x	5.6974	0.755679
298.1 ln ( )	= x log ( )	686.40	2.836578
298.1 R′ ln ( )	= x log ( )	1364.9	3.135106
298.1 ln 298.1	= x	1698.4	3.230041
298.1 (R/F) ln ( )	= x log ( )	0.05915	8.771988

BERKELEY, CAL.

A METHOD OF FINDING THE PARTIAL FROM THE TOTAL VAPOR PRESSURES OF BINARY MIXTURES, AND A THEORY OF FRACTIONAL DISTILLATION.

BY M. A. ROSANOFF, C. W. BACON AND JOHN F. W. SCHULZE.[1]

Section 1. A Relationship between the Total and Partial Pressures of Binary Mixtures.

A simple method of measuring the partial vapor pressures of liquid mixtures was described in another joint communication from these laboratories.[2] The method depends upon the analysis of a series of consecutive distillates from a given mixture, and presents no manipulative difficulties. The fractions are "analyzed" by determining their refractive indices[3] or, in the case of ternary mixtures, by determining the index of refraction and one other physical property, such as the density or the boiling temperature.[4] There are important cases, however, where mixtures cannot be so simply analyzed with any degree of accuracy, and consequently the experimental determination of the partial pressures would be unreliable.

[1] A brief preliminary account of the contents of this paper was published in the J. Frank. Inst., December, 1911.

[2] Rosanoff, Bacon and White, THIS JOURNAL, 36, 1803 (1914).

[3] v. Zawidzki, Z. physik. Chem., 35, 138 (1900); Rosanoff and Easley, THIS JOURNAL, 31, 968 (1909).

[4] Schulze, Ibid., 36, 498 (1914).

That partial pressures can be *calculated* from the total pressures (which are always readily determinable) has been pointed out by Margules.[1] But Margules's method, which depends on the graphic measurement of the slope of the total pressure curve at its two ends, is liable to yield inaccurate results. At best, it permits of finding only two constants for the calculation of partial pressures, and this is often insufficient.[2] For these reasons, and also with a view to the development of a mathematical theory of fractional distillation, it seemed desirable to formulate a general relationship, even if only empirical, between the total and partial vapor pressures.

Such a relationship is suggested by Konowalow's semi-quantitative principles relating to the shape of the total pressure curve.[3] These principles indicate that the greater the slope of the total pressure curve, the greater is the difference in composition between the liquid and its vapor. When the total pressure curve passes through a maximum or a minimum, its slope is zero, and the composition of vapor and liquid is identical. Calling x the molar fraction of one of the components in the liquid, π the total pressure, and p_1 and p_2 the partial pressures, we thus have: when $d\pi/dx = 0$, $(p_1/p_2)/[x/(1-x)] = 1$. This theorem suggested formulating the slope of the total pressure curve as *a logarithmic function of the relative composition of vapor and liquid.*

If, now, in a given case—for instance, in one of the cases discussed below— a set of values of $d\pi/dx$ are plotted against the corresponding values of $\log$ $[p_1(1-x)/p_2 x]$, *the result is found to be a straight line passing through the origin of the coördinates, which indicates that the simplest possible relationship exists between the two quantities: viz., proportionality.* This apparently general law is expressed by the equation:

$$d\pi/dx = (1/k) \log [p_1(1-x)/p_2 x]$$

The constant $1/k$ is evaluated by the following considerations: If the equation just given is applicable generally, it must hold true also in those cases in which the total and partial pressure curves are straight lines. In such cases $d\pi/dx = P_1 - P_2$ (the difference of the vapor pressures of the isolated components), and $[p_1(1-x)]/p_2 x = P_1/P_2$. We should, therefore, have:

$$d\pi/dx = P_1 - P_2 = (1/k) \log [p_1(1-x)/p_2 x] = (1/k) \log (P_1/P_2)$$

whence,

$$(1/k) = (P_1 - P_2)/(\log P_1 - \log P_2)$$

In general, then, we obtain:

$$d\pi/dx = [(P_1 - P_2)/(\log P_1 - \log P_2)] \log [p_1(1-x)/p_2 x] \quad \text{(A)}$$

[1] Margules, *Sitsb. Kais. Akad. Wiss. Wien.*, [2] **104**, 1243 (1895).
[2] See Rosanoff and Easley, *loc. cit.*, p. 957.
[3] Konowalow, *Wied. Ann.*, **14**, 34, 219 (1881).

The complete correspondence between Equation A and the qualitative theorems of Konowalow imparts to the equation something of a theoretical character. Also, (A) is at least not in conflict with the thermodynamic equation of Duhem and Margules. But its chief recommendation is that it faithfully reproduces·the experimental results in all known types of cases. Tables I, ard III show how closely it has permitted of calculating the vapor compositions from the total pressures, in three cases experimentally studied by v. Zawidzki.[1] Table IV relates to a case in which it has rendered valuable practical service, as explained further on.

In the tables below the composition of the liquids is expressed, not in molar fractions, but in molar *per cents.*, further, the partial pressures, which are directly dependent upon the composition of the vapor, are replaced by the corresponding molar per cents. in the vapor.

Case 1. Carbon Tetrachloride and Benzene —The isothermal total pressure curve for 49.99°, on the basis of Zawidzki's measurements, is well represented by the following equation, obtained by us with the aid of the method of least squares:

$$\pi = 268.075 + 80.853x - 43.826x^2 + 16.531x^3 - 13.695x^4$$

According to this equation,[2] a mixture containing 91.65 molar per cent. of carbon tetrachloride has a vapor pressure of 308.43 mm., which is a maximum, the vapor pressure of pure carbon tetrachloride being 308.0. Further, according to the equation:

$$\frac{\log_{10} P_1 - \log_{10} P_2}{P_1 - P_2} = 0.0015103,$$

and therefore, by Equation A:

$$\log_{10}[p_1(1 - x)/p_2 x] = 0.122115 - 0.132383x + 0.0749000x^2 - 0.082734x^3$$

The following table compares the results yielded by these equations with those found by Zawidzki experimentally. The second and third columns

TABLE I —CARBON TETRACHLORIDE—BENZENE

Molar % CCl4 in liquid	π obs mm	π calc	Molar % CCl4 in vapor	
			Obs	Calc
5 07	271 8	272 1	6 81	6 54
11 70	277 6	277 0	14 59	14 51
17 58	281 5	281 0	21 21	21 21
25 15	285 4	285 8	29 05	29 36
29 47	288 3	288 4	33 65	33 81
39 53	294 5	293 9	43 70	43 79
55 87	301 0	301 1	58 61	59 08
67 55	305 2	304 9	69 40	69 83
76 52	306 8	307 0	77 74	77 66

give the observed and the calculated total pressures; the fourth and fifth columns compare the experimental and the calculated molar percentages

[1] v. Zawidzki, *loc. cit.*

[2] See also Young, "Fractional Distillation" (London, 1903), p. 65.

of carbon tetrachloride in the vapor. The differences between experiment and our calculations are insignificant.

Case 2. Ethyl Iodide and Ethyl Acetate.—The isothermal total pressure curve (49.99°) is represented by the equation:

$$\pi = 280.325 + 250.403x - 285.085x^2 + 210.995x^3 - 103.147x^4$$

Accordingly, the curve passes through a maximum when the molar per cent. of ethyl iodide in the liquid is 76.49. Further,

$$\frac{P_1 - P_2}{\log_{10} P_1 - \log_{10} P_2} = 726.456,$$

and hence, by Equation A:

$$\log_{10}[p_1(1 - x)/p_2 x] = 0.344691 - 0.784865x + 0.871333x^2 - 0.567946x^3$$

TABLE II.—ETHYL IODIDE—ETHYL ACETATE.

Molar % C₂H₅I in liquid.	π obs.	π calc.	Molar % C₂H₅I in vapor.	
			Obs.	Calc.
5.90	294.3	294.1	9.8	11.1
11.48	304.7	305.3	17.7	19.3
13.76	308.7	309.9	20.9	20.1
19.46	319.5	319.7	27.9	28.6
22.88	325.2	324.9	31.7	32.2
30.57	335.4	335.4	39.0	39.4
37.45	343.4	343.2	45.3	45.4
45.88	350.7	351.0	52.2	52.4
54.86	357.4	357.4	59.7	59.5
63.40	361.7	361.6	66.1	66.1
73.88	363.5	364.1	74.0	74.4
82.53	363.5	363.6	81.5	81.5
90.98	360.7	360.4	89.3	89.4

Case 3. Chloroform and Acetone.—The isothermal total pressure curve (35.17°) is represented by the equation:

$$\pi = 343.719 - 146.168x - 418.752x^2 + 895.099x^3 - 380.240x^4$$

Therefore,

$$\frac{P_1 - P_2}{\log_{10} P_1 - \log_{10} P_2} = 732.3,$$

and, according to Equation A:

$$\log_{10}[p_1(1 - x)/p_2 x] = -0.199592 - 1.14361x + 3.66677x^2 - 2.07687x^3$$

In the case of chloroform and acetone there can be little doubt as to complex molecules being formed to a greater or less extent. Therefore, the agreement between the calculated and the experimental molar per cents., while not as close as in the preceding cases, may still be considered very satisfactory.

Case 4. Benzene and Toluene.—In this case the refractive indices of the two pure substances are not sufficiently different to permit of determining the composition of a given mixture refractometrically with any

degree of precision. Therefore, at least when the available amount of substance is small, experiment can only yield rough results. A need having arisen here (in connection with a study of isopiestic fractional

TABLE III.—CHLOROFORM—ACETONE.

Molar % CHCl₃ in liquid.	π obs.	π calc.	Molar % CHCl₃ in vapor.	
			Obs.	Calc.
0	344.5	343.7		
6.03	332.1	333.6	2.8	3.4
12.03	320.1	321.6	6.2	6.6
12.32	319.7	320.9	6.4	6.8
18.18	308.0	308.3	10.3	10.1
29.10	285.7	285.1	19.4	18.0
40.50	266.9	265.1	31.8	30.1
50.83	252.9	253.4	45.6	44.7
58.12	248.4	249.7	56.3	56.2
66.35	249.2	250.2	68.3	68.8
79.97	261.9	261.3	85.7	85 5
80.47	262.6	261.9	85.4	86.0
91.79	279.5	279.0	95.0	95.0
100	293.1	293.7		

distillation) to obtain accurate knowledge of the vapors given off by benzene-toluene mixtures, we felt that the mathematical method described above would lead to decidedly better results than any experimental method. The vapor compositions thus found corresponded to liquid mixtures kept at one and the same temperature. From these, however, we had no trouble in calculating also the composition of vapors given off by mixtures boiling isopiestically. We reproduce these calculations both as an illustration of the procedure involved, and because of the intrinsic value of the results.

Thiophene-free benzene and pure toluene were further purified by washing with water, drying with calcium chloride, and fractionating. The utilized fraction of either substance distilled over within 0.1°. A set of ten different mixtures was then accurately made up by weighing, and the total vapor pressures of these, as well as of the two pure substances, all at 79.70°, were determined with the aid of an Oddo ebullioscope connected by *wide tubing* with an empty tank and a baromanometer.[1] The measurements, which are recorded in the second column of Table IV, are almost perfectly reproduced by the following equation:

$$\pi = 288.438 + 466.519x - 56.464x^2 + 100.281x^3 - 49.971x^4$$

where x is the molar fraction of benzene in the liquid. The values of π given by this equation are reproduced in the third column of the table. This equation also gives:

[1] See Rosanoff and Dunphy, THIS JOURNAL, **36**, 1416 (1914).

$$\frac{\log_{10} P_1 - \log_{10} P_2}{P_1 - P_2} = 0.000900,$$

and consequently, according to our Equation A:

$$\log_{10}[p_1(1 - x)/p_2x] = 0.4198671 - 0.101635x + 0.270759x^2 - 0.179896x^3$$

The values of p_1 (partial pressure of benzene in the vapor) calculated from this last equation were converted into molar per cents. and are recorded as such in the fourth column of Table IV.

TABLE IV —BENZENE—TOLUENE (ISOTHERMAL).

Molar % of C₆H₆ in liquid.	π obs.	π calc	Molar % of C₆H₆ in vapor
100	748 7	748 8	100
95 65	729 0	728 9	98 27
91 89	711 4	711 6	96 72
82 43	668 0	667 7	92 49
73 27	624 9	625 0	87 82
63 44	579 2	579 2	81 97
54 51	537 5	537 8	75 74
43 52	487 0	487 2	66 56
33 83	443 1	443 0	56 76
22 71	392 8	392 5	42 95
11.61	341 5	342 0	25 30
0	288 5	288 4	0

With a view to the needs of our distillation study, we next proceeded to calculate the composition of the vapors as given off by the liquid mixtures boiling under *constant pressure*. But first the boiling temperatures themselves were determined, under a pressure of 750 ± 1 mm. Only in the case of the two isolated components the atmospheric pressure was higher, but not sufficiently so to affect the final results. These boiling temperatures are shown in the second column of Table V.

To find the vapor compositions at these temperatures, we made use of a principle introduced in an earlier communication.[1] In general, namely, the composition of vapors from binary mixtures may be accurately represented by an expression of the following form:

$$\ln \frac{p_1(1 - x)}{p_2 x} = \ln \frac{P_1}{P_2} + \alpha_2[(1 - x) - {}^1/_2] +$$
$$\frac{\alpha_3}{2}[(1 - x)^2 - {}^1/_3] + \frac{\alpha_4}{3}[(1 - x)^3 - {}^1/_4]$$

As shown in the communication referred to, the coefficients α_2, α_3, and α_4 are, in all cases in which the heat of dilution is moderate, practically independent of the temperature, so that changes of temperature influence the vapor composition only by affecting the value of P_1/P_2. If, therefore, from an expression found for some given temperature we should subtract the logarithm of P_1/P_2 corresponding to that temperature, and to the

[1] Rosanoff and Easley, THIS JOURNAL, 31, 957 (1909).

remainder add an expression representing the logarithm of P_1/P_2 as a function of the temperature, we should obtain a more general expression, from which the vapor composition could be calculated for any temperature or temperatures within the given range.

In the case of benzene and toluene the heat of dilution is very small, and therefore the principle just stated may, within the temperature range involved, be applied without hesitation. On the basis of both Regnault's[1] and Young's[2] measurements of the vapor pressures of benzene, and of Kahlbaum's[3] measurements of the vapor pressures of toluene, we find·

$$P_2/P_1 = 0.2641 + 0.001506t$$

where t is the centigrade temperature, the formula applying between 80° and 110°. For the temperature of our isothermal measurements, viz., 79.70°, and using common logarithms, $\log_{10}(P_2/P_1) = 0.4155238$ Subtracting this from 0.4198671, the constant term of our isothermal equation, and further, introducing, with the appropriate sign, the common logarithm of P_2/P_1 as a function of the temperature, we finally obtain:

$$\log_{10}[p_1(1 - x)/p_2 x] = 0.0043433 - 0.101635x +$$
$$0.270759x^2 - 0.179896x^3 - \log_{10}(0.2641 \quad 0.001506t)$$

The composition of the vapors from the mixtures indicated by the first column of Table V, at the temperatures given in the second column, were calculated by this final equation, and are recorded in the third column.

TABLE V —BENZENE—TOLUENE (ISOPIESTIC)

Molar % of C₆H₆ in liquid	Boiling point under 750 mm	Molar % of C₆H₆ in the vapor	Weight per cent of benzene	
			in the liquid	in the vapor
0	109 59°		0	0
10	104 85	20 8	8 6	18 1
20	101 00	37 2	17 5	33 4
30	97 55	50 7	26 7	46 5
40	94 60	61 9	36 1	57 9
50	91 85	71 3	45 9	67 7
60	89 30	79 1	56 0	76 2
70	86 85	85 7	66 4	83 5
80	84 55	91 2	77 2	89 7
90	82 25	95 9	88 4	95 1
95	81 00	98 0	94 2	97 7
100	79 70		100	100

In spite of the circuitous calculation, we believe these results to be quite exact. For convenience of reference, we add a fourth and fifth columns, expressing the same results in terms of per cents. by weight.

[1] Regnault, *Mem. de l'Acad*, **26**, 339 (1862)
[2] Young, *J. Chem. Soc*, **55**, 486 (1889)
[3] Kahlbaum, *Z physik Chem*, **26**, 603 (1898)

Section 2.   A Theory of Fractional Distillation without Reflux Condensation.

In principle, two different ways must be distinguished in which fractional distillation may be carried on: the vapor may either be allowed to escape from the still without any reflux condensation at all, or else it may be partially recondensed on its way, the condensate returning to the boiling liquid in the still.   In all practical work, whether on a laboratory or an industrial scale, partial reflux condensation is employed invariably, because it greatly increases the efficiency of the process by increasing the difference between the composition of the vapor and that of the boiling liquid.   A rational process of this type will shortly be described in a special series of publications.   In this present communication we will consider only distillation involving no reflux condensation—a process, to be sure, of academic rather than of practical interest, but nevertheless worthy of consideration.

Since the appearance of Konowalow's classic paper[1] on the total vapor pressures of mixtures, it has been clearly understood that in all cases, except where the vapor pressure of the given mixture is a maximum or a minimum, distillation divides a mixture into fractions of unequal volatility, the residue being less volatile than the distillate and even less volatile than the original mixture.   In other words, during a distillation at constant temperature the total pressure of the liquid in the still must continually diminish; during a distillation under constant pressure, the temperature of the boiling mixture must continually rise.   But these Konowalow principles, being purely qualitative, do not constitute a theory of distillation in the truer sense of the term.   A true theory of distillation should furnish a general answer to questions like the following: given a mixture of a certain specified composition, what proportion by weight of the total must be distilled off in order that the composition may change from what it was originally to some new specified value?

An attempt to solve this problem was made some twenty years ago by Barrell, Thomas, and Young.[2]   The assumption underlying their solution is that throughout the distillation the ratio of the weights of the components in the vapor is proportional to the ratio of the weights in the liquid.   Denoting by ξ and η the weights in the liquid, and by $d\xi$ and $d\eta$ the weights in the vapor, the assumption is expressed by the equation:

$$d\xi/d\eta = c.\xi/\eta$$

or

$$d\ln\xi/d\ln\eta = c,$$

[1] Konowalow, *Wied. Ann.*, **14**, 34, 219 (1881).

[2] Barrell, Thomas and Young, *Phil. Mag.*, [5] **37**, 8 (1894); Young," Fractional Distillation" (London, 1903), p. 93; Nernst, *Theoretische Chemie* (Ed. 7, Stuttgart, 1913) p. 109.

c being a constant. This assumption had some years previously been proposed by F. D. Brown.[1] But, as Young himself has pointed out in his monograph on fractional distillation, Brown's assumption cannot possibly be true as a general rule, and leads to absurdities in those cases in which the total pressure curve passes through a maximum or a minimum. It must, however, be added that Brown's formula does hold good for the isothermal distillation of mixtures whose partial and total vapor pressure curves are perfect straight lines; only such cases are rare.

Another theory of distillation was proposed in 1902 by Lord Rayleigh.[2] Let the weight of a given liquid mixture be denoted by w, and the weight of the first component in it by y. Then y/w is the fraction of the total weight constituted by the first component. If this fraction is denoted by ξ, we have: $y/w = \xi$, or

$$y = w\xi$$

Let, at the same time, the entire weight of the vapor be dw, and the weight of the first component in the vapor dy. Then the fraction by weight of the first component in the vapor is dy/dw. In any given case the fraction of the first component in the vapor will be some function of the fraction in the liquid:

$$\frac{dy}{dw} = f(\xi),$$

or since $y = w\xi$

$$\frac{d(w\xi)}{dw} = f(\xi),$$

whence, if w_0 and ξ_0 denote the initial values of w and ξ,

$$\ln \frac{w}{w_0} = \int_{\xi_0}^{\xi} \frac{d\xi}{f(\xi) - \xi}$$

To turn this mode of formulation into a theory, it is necessary to make some assumption regarding the nature of the function $f(\xi)$. Lord Rayleigh assumes that *in very dilute solutions*, *i. e.*, in mixtures containing very little of what we call the first component, the fraction of that component in the vapor is simply proportional to its fraction in the liquid: $dy/dw = f(\xi) = \kappa\xi$; whence, by integration,

$$\xi/\xi_0 = (w/w_0)^{\kappa - 1},$$

the constant κ to be found empirically.

. Lord Rayleigh's theory is thus confined to very dilute mixtures only and leaves room for a more general theory, based on some reliable assumption regarding the relation between the composition of the vapor and of the liquid for all possible concentrations. Such a relationship, even if only

[1] Brown, *Trans. Chem. Soc.*, **39**, 317 (1881).

[2] Lord Rayleigh, *Phil. Mag.*, [5] **4**, 527 (1902); see also Plucker, *Pogg. Ann.*, **92**, 198 (1854).

semi-theoretical in character, is furnished by Equation A developed in the preceding section; and as that equation appears to hold true in all types of cases, a mathematical theory of distillation based upon it must likewise be generally applicable.

As in connection with the Brown formula above, we will again denote by ξ and η the absolute weights of the components in the liquid, and by $d\xi$ and $d\eta$ their absolute weights in the vapor. Let, further, p_1 and p_2 represent the partial pressures of the components, and let x represent the molar fraction of the first component in the liquid. Then p_1/p_2, the ratio of the partial pressures, equals the ratio of the molar fractions in the vapor, these molar fractions being based, of course, on the actual molecular weights of the two vapors. But, as pointed out in a previous communication,[1] if the purely thermodynamic equation of Duhem and Margules is not to be contradicted, the molar fractions x and $1 - x$ in the liquid must be based on the same molecular weights as the molar fractions in the vapor. It may, therefore, be stated with certainty, that the quotient of the ratios of the *molar fractions* in vapor and liquid is equal to the quotient of the ratios of the weights, as expressed by the equation:

$$\frac{p_1(1-x)}{p_2 x} = \frac{\eta d\xi}{\xi d\eta},$$

or

$$\frac{d \ln \xi}{d \ln \eta} = \frac{p_1(1-x)}{p_2 x}$$

Now, our Equation A teaches that

$$\log \frac{p_1(1-x)}{p_2 x} = k \frac{d\pi}{dx},$$

or

$$\frac{p_1(1-x)}{p_2 x} = e^{kd\pi/dx},$$

e denoting, as usual, the base of natural logarithms. We therefore have:

$$\frac{d \ln \xi}{d \ln \eta} = e^{kd\pi/dx} \quad \dots \dots \dots \dots \dots (B)$$

and all conclusions regarding the course of a fractional distillation based on this formula will be as reliable as Equation A itself.

Calling M_1 and M_2 the molecular weights of the two components, we have:

$$\frac{x}{1-x} = \frac{\xi/M_1}{\eta/M_2},$$

whence

$$d \ln(\xi/\eta) = dx/x(1-x)$$

and

$$d \ln \eta = d \ln \xi - dx/x(1-x)$$

[1] Rosanoff, THIS JOURNAL, 36, 1410 (1914).

Then, by simple transformation, from (B):

$$d \ln \xi = \frac{e^{kd\pi/dx}}{(e^{kd\pi/dx} - 1)(1 - x)x}\, dx$$

Denoting by ξ_0 and x_0 the initial weight and the initial molar fraction of the first component in the liquid, we get

$$\ln \frac{\xi}{\xi_0} = \int_{x_0}^{x} \frac{e^{kd\pi/dx}}{(e^{kd\pi/dx} - 1)(1 - x)x} \cdot dx \dots \dots \dots \dots (C)$$

For the second component we obtain analogously:

$$\ln \frac{\eta}{\eta_0} = \int_{x_0}^{x} \frac{dx}{(e^{kd\pi/dx} - 1)(1 - x)x} \dots \dots \dots \dots (D)$$

Needless to say, the integrations may be readily carried out by one of the ordinary approximation methods. Also, only one of these integrations must be carried out, as the quantities ξ and η are connected by the equation:

$$\eta = \frac{1 - x}{x} \cdot \frac{M_2}{M_1} \cdot \xi$$

It will be noted that Equations C and D express the relation between the changes of weight and composition accompanying isothermal fractional distillation, in terms of $d\pi/dx$, the slope of the total pressure curve. They may thus be regarded as an attempt at a quantitative formulation of the Konowalow theory of distillation.

In the rare cases in which the total and partial pressure curves are straight lines, our theory becomes essentially identical with the Brown-Young theory of distillation. Since $d\pi/dx$ is then constant ($= P_1 - P_2$), our Equation B turns into the Brown formula:

$$\frac{d \ln \xi}{d \ln \eta} = \frac{P_1}{P_2} = \text{constant},$$

and the integrals in (C) and (D) assume the values:

$$\frac{\xi}{\xi_0} = \left[\frac{x(1 - x_0)}{x_0(1 - x)}\right]^{P_1/(P_1 - P_2)}$$

and

$$\frac{\eta}{\eta_0} = \left[\frac{x(1 - x_0)}{x_0(1 - x)}\right]^{P_2/(P_1 - P_2)}$$

It is easy to read into these last equations that if the total pressure line were parallel to the x axis, so that $P_1 = P_2$, then no matter what weight were distilled off from the original mixture, the composition would remain unaltered: $x/(1 - x) = x_0/(1 - x_0)$, as must of course be the case.

The theory, in the form of Equations C and D, has been tested out here by direct experiment. It would, however, be superfluous to publish the results, seeing that the theory is based on no other principles than those involved in Equation A, and that the validity of the latter is, sufficiently indicated by the cases discussed in the preceding section.

In conclusion, we will mention that the above is one of a series of studies (mostly experimental) that have been made possible by a grant from the Rumford Fund of the American Academy of Arts and Sciences. It is a pleasure to again express our thanks to the Rumford Committee for their generous interest in this work.

WORCESTER, MASS.

PASSIVITY OF METALS.

BY HORACE G. BYERS AND SETH C. LANGDON.

Introduction.

In a previous paper by one of us,[1] the term passivity was defined as properly applying to an element when it "shows abnormal electrochemical relations, and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electromotive series of the elements." These characteristics are exhibited by a number of elements under a variety of circumstances and to varying degrees, but the passivity of iron has been most carefully studied and the present paper is limited to a study of one phase of its behavior. Iron becomes passive when immersed in certain electrolytes, which are always oxygen compounds. It also becomes passive under certain conditions when used as an anode. In this case also, the electrolyte is almost always an oxygen compound in solution in water. The most apparent evidences of transition from the active to passive condition of iron, as an anode, are: the metal no longer dissolves, its surface brightens, oxygen is evolved from its surface and, coincident with these changes, an ammeter, in series in the circuit, shows a sudden drop in the current. Considerable work has been done in this laboratory on this behavior and the conclusion reached,[2] that the following factors influence the establishment of the passive state in iron used as an anode: (a) the character and condition of the metal; (b) the electrolyte employed; (c) the temperature; (d) the curent *density;* (e) the duration of passage of the current; and (f) the character of movement of the electrolyte.

In the hope that the above variables represented a complete catalogue, it was thought that light could be thrown upon the subject by a study of the behavior of an anode when *two of the factors were allowed to vary mutually while all others were held constant.* Below, is given, briefly, the experi-

[1] THIS JOURNAL, **30,** 1718 (1908).

[2] *Ibid.,* **35,** 759 (1913).

mental method employed and results obtained when the attempt was made to determine the relation between the current density and the time required to induce passivity.

Experimental.

The arrangement of the apparatus is shown in Fig. 1. The electrolyte used was 0.2 N sulfuric acid contained in a small glass cell immersed in ice water. The anode was a piece of iron wire "for standardization," diameter 0.720 mm., sealed with paraffin into a glass tube so that a length of exactly 10 mm. was exposed. The cathode was a platinum wire sealed in a glass tube. The electrodes were connected in series with six storage batteries, a resistance box, a Weston milliameter and a key.

The external resistance is first adjusted so that a current of the required density will flow through the circuit, and the time required to convert an active anode to the passive condition is determined by a stop-watch, the time recorded being the interval between the closing of the
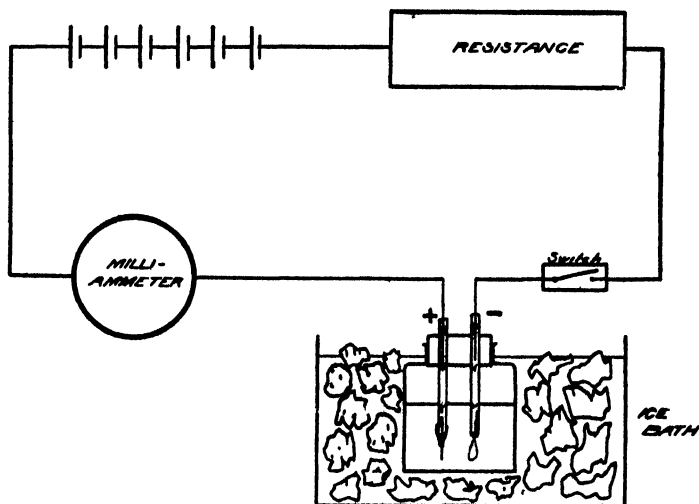
Fig. 1.

key and the appearance of the phenomena above described. If the current be not too small, the time required is fairly small and, therefore, iron is dissolved to an extent insufficient to materially affect the diameter of the wire. It was, therefore, possible to make a series of determinations on one section of wire. In order that these should be comparable, the circuit was broken as soon as the iron became passive and allowed to remain open 30 seconds before closing the circuit for the next determination. This interval is quite sufficient for, in 0.2 N sulfuric acid, iron rendered

passive as an anode almost instantly becomes active when the current is stopped. The character of the results is shown in Table I.

TABLE I

0 2 N H_2SO_4, temperature, 0°, 10 mm wire exposed

Milliamperes current	Time in seconds to passivify the iron	Diameter of the wire.
30	12	0 709
30	22	0 707
30	24	0 705
30	26	0 703
30	25	0 797
30	28	0 695
30	28	0 693
30	30	0 687
30	29	0 685
30	29	0 680
30	38	0 675
30	31	0 670

Disregarding the first determination, there is a range of difference from the mean time of 28 seconds which is not to be accounted for by the small variation of current density due to change in the surface of the wire exposed. A large number of similar determinations were made, using current densities ranging from 15 to 80 milliamperes with a corresponding time required to passivify the iron varying from 21 minutes to 3 seconds. All experiments showed a similar lack of agreement between individual measurements. Sets of determinations were also made at 18° and at 25°, using the cell in a thermostat. These gave even less satisfactory results, due, in part, to the greater loss of iron while rendering the anode passive, greater current densities being needed at higher temperatures. These somewhat extended experiments failed to show the desired uniformity of relation between two variables and the suspicion that all the factors influencing the passive condition were not yet at hand grew more pronounced.
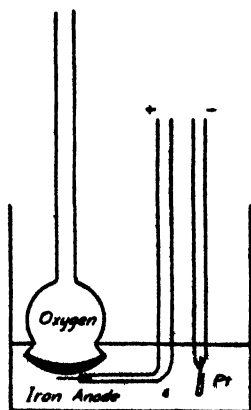
During the progress of the work it was noted that minute bubbles of oxygen occasionally adhered to the surface of the iron even after it became wholly active and that in such cases the metal became passive more readily. Jarring the electrode, or stirring the electrolyte, partially obviated this difficulty, but when minute bubbles were allowed to persist, the results still varied widely. This suggested that *dissolved* oxygen in the neighborhood of the electrode might be a factor in our problem.

Fig 2.

To test the question an apparatus, Fig. 2, was so arranged that the iron anode could be held close beneath an atmosphere of oxygen which was kept at constant pressure in the thistle tube. By rotating tube bearing the anode, it could be readily removed somewhat distant from this concentration of oxygen. The results obtained (Table II) indicate clearly that iron is much more readily made passive near the oxygen surface. When hydrogen gas or nitrogen was substituted for oxygen no such effect was produced.

TABLE II

$N/5$ H_2SO_4, room temperature, 5 mm iron wire exposed

No	Time in sec for 30 m amps to passivify	Diam of wire in mm	Relation of iron to oxygen bubbles	No	Time in sec for 30 m amps to passivify.	Diam of wire in mm	Relation of iron to oxygen bubbles
1	10	0 710	Under	13	37	0 700	Not under
2	11	0 709	Under	14	17	0 700	Under
3	16	0 708	Under	15	23	0 700	Under
4	17	0 708	Under	16	24	0 697	Under
5	13	0 708	Under	17	45	0 693	Not under
6	13	0 707	Under	18	19	0 693	Under
7	27	0 706	Not under	19	47	0 692	Not under
8	26	0 706	Not under	20	25	0 688	Under
9	15	0 705	Under	21	63	0 688	Not under
10	22	0 705	Under	22	30	0 680	Under
11	22	0 704	Under				
12	20	0 702	Under				

Nos 3–6 show an average a little above 15 seconds
Nos 7 and 8 not under the oxygen required about twice the time
No 9 under the oxygen, goes down to 15 seconds again
After No 9, the iron was removed from the electrolyte, washed and dried and the experiment discontinued for about 20–25 minutes and after this more time was required to render the iron passive but in general the time required under the oxygen was about half that required when not directly under the bubble of oxygen

The effect of higher concentrations of oxygen was next investigated with the apparatus arranged as in Figs. 3 and 4. A tank of oxygen was connected to a manometer and thence to the cell, which was closed by a rubber stopper held in place by a pressure clamp. The anode and cathode were arranged as before, except that the anode was held in place by Khotenski's wax and then coated with paraffin. A length of 5 mm. was exposed. The electrical connections were as before. The cell was placed in an ice bath not shown in the cut. All factors known to influence passivity were thus held constant except the concentration of the oxygen above, and consequently in, the solution. After a desired oxygen pressure had been established and sufficient time to secure saturation had elapsed, the cell was shaken with a circular motion to insure freedom from anode bubbles. After 30 seconds the circuit was closed and the time required for a current of 15 milliamperes to passivify the iron was measured. The circuit was then opened and measurements repeated. Table III shows

TABLE III.

No.	Time in seconds to passivify the iron.	Oxygen pressure in pounds per square inch.	No.	Time in seconds to passivify the iron.	Oxygen pressure in pounds per square inch.
1.......	?	air that is oxygen, 3 pounds	18......	7	
2.......	40		19......	6¹/₂	
3.......	45		20......	7	57.4 pounds
4.......	45		21......	6¹/₂	
5.......	45		22......	7	
6.......	20		23......	5	
7.......	21		24......	6	
8.......	22	15 pounds	25......	5	65.88 pounds
9.......	20		26......	5	
10.......	20		27......	4	
11.......	12		28......	4¹/₂	
12.......	11		29......	5	81.34 pounds
13.......	12		30......	4	
14.......	10¹/₂	51 pounds	31......	4	
15.......	11		32......	34	Here fresh electro-
16.......	11		33......	45	lyte substituted.
17.......	11		34......	45	Saturated with air, i. e., oxygen, 3 pounds

0.2 N sulfuric acid. 5 mm. length of iron wire exposed. Initial diameter 0 710 mm. Final diameter 0 680 mm. 15 ma. current employed while rendering iron passive.

such a series for pressures of oxygen ranging from 3 lbs. per sq. in. to 81 lbs. with one section of wire. The values so obtained represent a very satisfactory constancy and are typical of a large number of series which are not detailed.
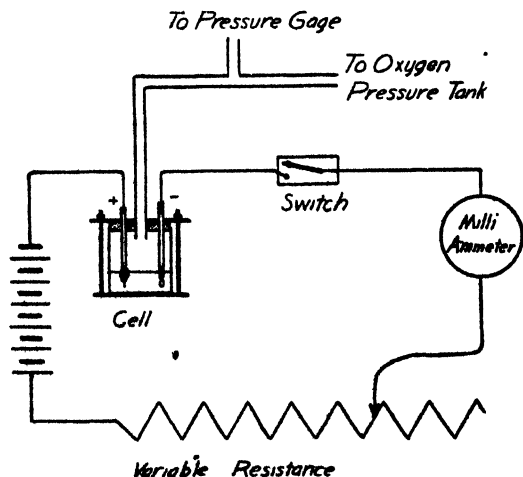
It will be observed that loss of surface area, due to solution of the iron, is not a seriously disturbing factor since the decrease of diameter of the iron in successive determinations is about 0.0009 mm., and only 0.03 mm. in the whole series of 34 determinations. When oxygen pressures of 0.2

Fig. 3

atmosphere, secured by air pressure were used no such uniform agreement in time, required to render iron passive, could be obtained. This accounts to us fully for our long-continued failure to secure quantitative results under atmospheric pressures. When 0.2 N nitric acid was used as the electrolyte, other conditions being otherwise the same as those above detailed, the results were different; the iron becomes active much less readily in nitric acid. It was finally found necessary to remove the iron after each determination, wash with 0.2 N sulfuric acid and with water before a satisfactory repetition could be obtained. With nitric acid also, the factor of continued passage of the current is less marked in its effect than with sulfuric acid, and a critical density is more apparent. Below this critical density, even long-continued passage of the current only infrequently produced passivity. If the current density is

Fig. 4.

sufficiently great, passivity is established practically instantly. For 0.2 N nitric acid solution at atmospheric pressure, $i. e.$, about 3 lbs. per sq. in. of oxygen pressure, the critical current was found to be 20 milliamperes. At 56 lbs. oxygen pressure, the critical current was 13 milliamperes. It will be observed that increase of oxygen pressure here lowers the current density required to render the iron passive.

In 0.01 N hydrochloric acid with 53 lbs. oxygen pressure, oxygen was evolved freely and the other phenomena of passivity appeared when the current density was relatively high. When the other conditions, except the pressure of gas imposed, were similar, there was only a very slight evolution of gas at the anode. With 0.02 N hydrochloric acid less oxygen was evolved, and with 0.05 N and 0.1 N solutions no indications of passivity either with or without oxygen pressure, could be observed. It appears that with a sufficient dilution of chlorine ions the passive state can be induced in halogen solutions: a fact not heretofore demonstrated.

Summary and Conclusions.

From the foregoing results it appears that to the six factors, mentioned in the introduction, which condition the passive state is to be added a seventh: The concentration of dissolved oxygen about the anode. Indeed, this is apparently *the* determining factor. When all these factors are taken into account, constant results are obtainable with respect to the
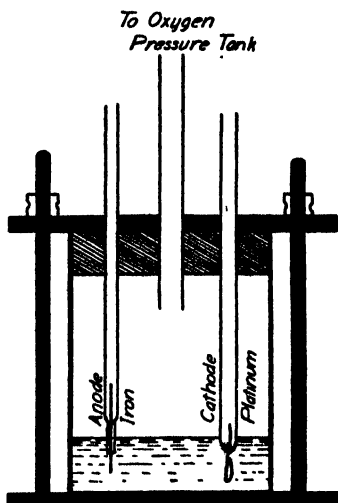
time required to render iron passive with a given current in sulfuric acid and in nitric acid a critical current density is determinable.

In a previous paper by one of us[1] it was stated that of the various theories concerning passivity none were satisfactory and that the writer had none to offer. It is desired here to formulate the ideas which have been developed by several years more or less of continuous investigation of the problem.

It would appear that of the various views offered several are correct so far as they go and for that reason were to a certain extent justified. The most satisfactory explanation of passivity is that furnished by Faraday —not the so-called Faraday explanation as perverted by Beetz and Wiedeman, but rather his statement that the state is one of a "very delicate equilibrium" between oxygen and iron. According to Le Blanc[2] iron has a limited rate of ionization at a given temperature. This may be taken as at least a reasonable hypothesis. If, now, a current is tending to leave an anode at a rate which requires solution of the metal, in accordance with Faraday's law, at a rate greater than the anode can ionize, then either the current pressure must increase the rate of ionization, anions must separate on the anode, or the current is retarded. If the anion is liberated and is of a type which when liberated covers the anode, one of two things occurs: 1st, When the anodic covering is highly non-conducting material, the current is cut off and the anodic deposition slows up or ceases. This is the type furnished by the reactions with cyanides, oxalates, etc. 2nd, In the case of compounds which readily liberate oxygen under anodic conditions, deposition of the gas on the surface takes place. When such deposition begins in effect, the surface of anode exposed is lessened and the rate of deposition is consequently increased. This explains the "spread of passivity" over an iron anode, which is a visible phenomenon. The anode being covered by a film of oxygen is no longer an iron anode but a gas electrode. The single potential measurements recorded by Schoch and others,[3] are then simply measurements of the potential of oxygen electrodes and have no relation whatever to the potential of iron itself.

It appears that oxygen *is occluded by the iron*. This conclusion is reached not alone from the fact that single potential measurements of iron and nickel, etc., when passive, are different but because maximum potentials are so reached. Also from an uncompleted investigation in this laboratory it appears that increase of oxygen pressure does not, at least at small pressures, increase the anodic potential shown by iron anodes.

The appearance of the passive condition on metals when they are simply immersed in electrolytes, as iron immersed in concentrated nitric acid,

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[1] *Loc. cit.*

[2] *Z. Elektrochem.*, **11**, 9 (1905).

[3] N. T. M. Wilsmore, *Z. physik. Chem.*, **35**, 291–332 (1900).

chromate solutions, etc., is to be accounted for by the presence of *pure oxygen* in these solutions. That such is the case is scarcely to be questioned if the principles of equilibrium reactions are taken into account. In the experimental portion of this paper it is shown that iron as an anode may be rendered passive in highly dilute hydrochloric acid. This is as it should be, when it is recalled that in the electrolysis of hydrochloric acid the proportion of oxygen liberated at the anode increases with dilution.

While the facts shown by Muthman, Heathcote and others, with respect to air or in a vacuum, argue strongly against the existence of an oxide film, they are to be expected if occluded oxygen is the real passive anode. It is, perhaps, not desirable to enter further upon a discussion designed to show how completely the facts accord with the view just presented, but we will content ourselves with a brief and clear restatement.

We consider passivity, not associated with a visible film, to be due to the rate of ionization of certain metals, being insufficient to carry currents of greater than certain densities. When such current density is exceeded, oxygen electrodes, consisting of occluded oxygen, are formed in oxygen electrolytes. Non-anodic passivity is likewise due to occlusion of oxygen and consequent protection of the metal from attack.

UNIVERSITY OF WASHINGTON

LEAKAGE PREVENTION BY SHIELDING, ESPECIALLY IN POTENTIOMETER SYSTEMS.

BY WALTER P WHITE.

This paper describes methods of making insulation more effective in electrical measuring systems by diminishing the influence of disturbing electromotive forces, both external and internal.

These methods, whose principles were known for at least ten years before their application to the potentiometer, are no more needed by the potentiometer than by other instruments of equal delicacy, but are exceptionally effective with it. They are not needed where insulation is quite adequate, as it usually is in dry weather, and an enormous amount of excellent work has certainly been accomplished without them, so that they are sometimes regarded, on first acquaintance, as an unnecessary complication. But in damp weather they have often proved both indispensable and very efficient, yielding results of the highest precision under conditions that would have been nearly hopeless without their aid; while as to complication, the arrangements, once installed, require no attention whatever, and the time of installation, an hour or two, is less than may be required to even locate one of the leakages that might occur through their absence.

The general principle of the methods appears most simply in the prevention of external leakage, that is, of disturbances due to stray currents

from heat, light, or power circuits, etc. Suppose, for instance, that as a result of leakage from 110 volt circuits the top of the table on which a thermoelement is situated is at a potential 60 volts different from a neighboring table, where stands the corresponding potentiometer (Fig. 2a). If insulation is at all defective a current will flow from one table to the other through the measuring system, and some of this will traverse the galvanometer, causing a false deflection. And since the maximum electromotive force of a thermoelement rarely exceeds 0.02 volt, the current due to 60 volts, even if very feeble for such an electromotive force, might be rather large compared to the thermoelement current. An insulation resistance of 5,000,000,000 ohms would usually be needed to prevent it from causing an error of 1 microvolt in the absence of some such arrangement as that to be described.

If Fig. 1 represents, in simplified fashion, the measuring system, and the leakage current enters and leaves by the two points A and B, the leakage deflection can be reduced in three ways:[1]
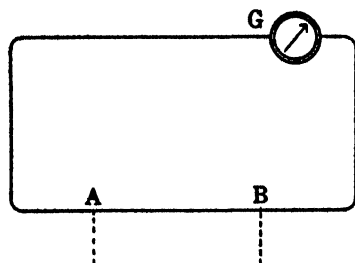
Fig. 1.—Circuit diagram.

(a) By improving the insulation. It is, of course, only where this cannot be done sufficiently that other methods are necessary.

(b) By diminishing the resistance A C B, so as to shunt the leakage current away from the galvanometer.

(c) By diminishing the external voltage between A and B.

The last can be accomplished by means of an *equipotential shield*. In the present instance this shield might be two sheets of tin plate, one covering each table, with a wire making connection between the two. The apparatus remains insulated from the plates, just as it was before from the tables. The essentials of the arrangement are shown in Fig. 2, which shows a measuring system first unshielded and then shielded. The leakage current from the exterior voltage cannot now reach the points A and B without first encountering the shield, and, since the shield is a very good conductor, the current will pass along it, but without producing in it any appreciable difference of potential. The shield therefore is an *equipotential* body, and the voltage available for producing a current between A and B has been reduced from 60 volts to a very small and quite negligible fraction of a volt. There is in this case no change in the resistance A B, and none is needed. The protection is practically absolute.

In general, the necessary and sufficient condition of this absolute pro-

[1] A discussion of these methods will be found in "Potentiometer Installation Especially for High Temperature and Thermoelectric Work," *Phys. Rev.*, 25, 340 (1907).

tection is that the shield should interpose itself between the measuring system and the environment at every point where leakage can occur Leakage ordinarily does not occur through the air, hence protection is needed only where solid bodies are in contact with the system, but in very hot furnaces, where the ionized air conducts, a practically complete boxing in is necessary for perfect protection. Of course electric lights, motors, etc., which may be on either of the tables of our illustrative case, must be shielded off, but this does not mean that the shield must be bent up so as actually to come between the light or motor and the potentiometer. It will do its work quite as well if the motors, etc., merely stand on it. As long as the current cannot reach the measuring system with-

(a)

(b)
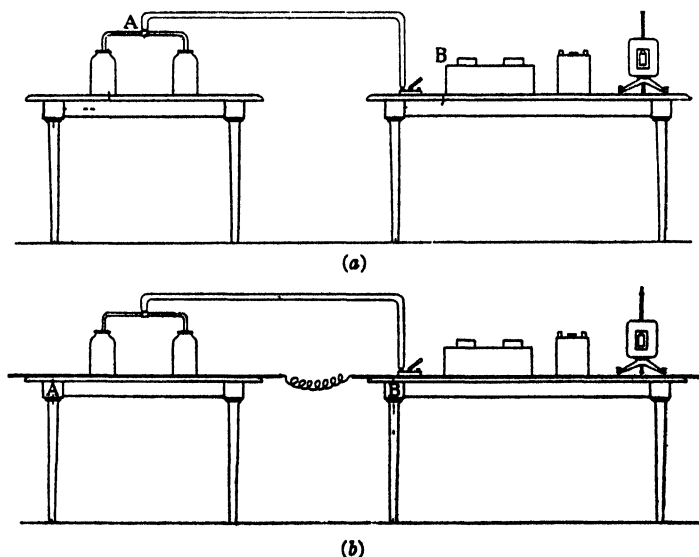
Fig. 2 —Diagram of possible leakage paths in (a) unshielded, (b) shielded, system of apparatus

out being conducted by the shield (whether through or along it makes no difference) the protection is complete.[1] This of course involves that the motors, etc., must not touch anything which also touches the measuring system, except the shield. For instance, if each is insulated from the shield by linoleum, the linoleum under the potentiometer must be a different piece from the other, otherwise a current might leak along the surface of the linoleum from motor to potentiometer, outflanking the shield. In most cases no trouble would result in this particular way, but this would be due to the insulating power of the linoleum, not to the shield, and the

[1] This necessity may perhaps be satisfactorily expressed by saying that the interposition must be *electrical* but not necessarily *geometrical*.

protection would not be so certain as with the insulating material in two separate pieces.

It may be supposed that the shield would be more effective if "earthed" by connecting (say) to a gas or water pipe, as in electrostatic experiments, but this use of the electrostatic analogy is quite misleading. In electrostatic work the lines of force are often important, and these may run to the walls of the room. These walls are really "the earth" for experiments within that room, and are often conveniently reached through a connection to the iron pipes. With the potentiometer system, on the other hand, all effects through or in the air are (ordinarily) quite negligible; the shield arranged as above described is, with the air, an absolutely complete enclosure as far as concerns the only thing—leakage currents—whose effect is to be prevented; the connecting of pipes or any other external thing to this shield cannot possibly be of any advantage electrically and may prove a harmful complication, introducing another source of leakage currents. *Mechanically,* a pipe system may sometimes prove convenient as part of the shield, and may then perhaps be justified in spite of its electrical disadvantages.

Failure is practically impossible with a properly arranged shield. A proper arrangement is more certain and permanent if the plan is simple, and the connecting wires well soldered, and stout enough to be secure from accidental rupture.[1] Of course those using the shielded apparatus should understand that the connecting of lighting circuits, etc., to anything inside the shield gives a chance for leakage trouble, and ought not to be done without first insuring that no detrimental leakage will result therefrom in that particular case. In the Geophysical Laboratory the tables have metal legs; connecting these legs into the shield shields the table top and everything on it. Wooden tables have been shielded by putting, between the legs and the floor, metal plates, connected to each other and to the rest of the shield by stout and stoutly fastened wires, running down the table legs. The connecting cables are suspended from overhead wires; connecting these wires into the shield shields the cables. Other apparatus is shielded by putting it on metal plates which are connected into the shield, sometimes by suspending it from wires similarly connected or—in the furnaces—by a more or less complete enclosure.

Shielding during Energy Measurements.

There are two cases where the simple and complete form of shield just described must or may be modified. One is where the high voltage circuit must be brought within the shield in order that the potentiometer

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[1] It will generally be worth while to arrange the shield so that all its parts are electrically in series, and so that connection can readily be made to the two ends of the line. The integrity of the whole shield can then be easily tested by seeing if a current readily passes through it.

may be used to make measurements upon it. Here the measuring system is kept at a definite potential by the connection with the power circuit, and so is not free to come to the potential of the shield. It is therefore necessary[1] to bring the shield to the potential of the measuring system, which is accomplished by connecting the shield directly to the high voltage circuit very near the point where the measuring system touches it. This insures that the potential of the shield shall not differ much from that of any part of the measuring system, which is, of course, the essential condition for effective shielding.

One other condition is generally necessary in this case. If the current through the measuring coil is that which passes through a heating coil (the commonest application in calorimetry of this sort of measurement), exactly the same current must pass both. This can be insured by connecting the shield to the high voltage circuit just *outside* the measuring connection, and not between measuring coil and heating coil, that is, at H, not K, in Fig. 3. Then stray currents passing to or from the heating circuit by way of the shield (such as may readily exist, and of relatively large magnitude) will pass around both the coils if they are going to the negative terminal, and through both if to the positive. The current through the heater, therefore, will be

Fig 3 —Protective connection for high voltage system within the shield. Correct from H, wrong from K

correctly measured by the voltage across the other coil, no matter where all of that current comes from. If the connection is to the point K, between the two coils, the same sort of leakage currents will always pass through one and around the other.[2]

Special Arrangements with Electric Furnaces.

In electric furnaces ionization gives the air a conductivity which increases rather rapidly from 1300° up. Shielding from the heating current therefore requires a conducting enclosure which must be practically complete in the furnace, though it need not be strictly air-tight Such an enclosure, of course, must usually be of platinum, and is therefore somewhat expensive, as well as often inconvenient. While it is nearly or quite essential for high precision (readings to 1 microvolt or better), it can well be omitted in general. In that case its place inside the furnace is taken by a loose spiral

[1] Necessary, that is, if any shielding is necessary. It is always true that where insulation is quite effective the shield is not needed, but the shield is used, and the present article applies in all cases where a reliance on insulation alone is impossible or undesired.

[2] Leakage to K from the other terminal, L, of the heating coil will evidently produce the same sort of error as a connection to K. It can be prevented by putting around L an arm of the shield, that is, a small shield connected to the main shield. Cf. "A Test of Calorimetric Accuracy," *Phys. Rev.*, **31**, 687 (1910).

of wire, which gives imperfect protection; but the effect of the shield may be supple-
mented by the other two methods of controlling leakage mentioned above, namely,
improvement of insulation, and shortening of the shorter leakage path in the circuit
(A B, Fig. 1).

The length of this shorter path is sometimes controlled by the conditions in the
furnace, when both A and B of Fig. 1 lie within the ionized region. Usually, however,
the leakage is found to increase in damp weather, which shows that one of the points,
say B, is out in the room, since of course the dampest weather does not affect the inside
of a furnace heated to 1300°. If, now, a point on the thermoelement just outside the
furnace is connected to the shield, the current which leaks into the thermoelement
inside the furnace (that is, at A) will run to the shield at once along the new connec-
tion, and no longer go on to the former point B. This particular arrangement has
sometimes proved useful, but generally fails, because, though it shortens A B of Fig.
1, it also increases the leakage current by providing an easier path for it. Two modi-
fications of the plan, however, are valuable. (a) In one the connection to the shield

_ To measuring
- instruments.
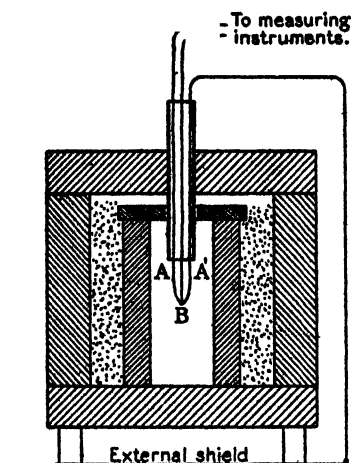
Fig. 4.—Fenner's method of shielding in elec-
tric furnaces.

runs into the furnace, and to the very
junction of the thermoelement[1] (Fig. 4).
Here, though the leakage path is good,
the distance A B is exceedingly short,
moreover for any leak from A to B
there is likely to be a nearly equal leak
from A' to B, whose effect on the
galvanometer is opposite[2] Experience
has shown this arrangement to work
very well. (b) The second modification
of the short connection plan gives a
short path A B, and at the same time
decreases the amount of leakage. It is
obtained by putting an internal shield
between most of the apparatus and the
external shield, making the short con-
nection to this internal shield, and then
insulating the whole arrangement. The
added insulation can consist of a few
hard rubber blocks, simple, accessible,
and easily made more effective, as a
rule, than the regular insulators of the

apparatus. The total leakage will thus be less. At the same time what there is will
have to traverse the shield, and hence will take the full metallic path to the shield.
This path will be a connection to one of the thermoelement leads, or to the negative poten-
tiometer terminal, hence the path A B will be short. Of course the internal shield
must cover all the points, wherever they are, at which leakage from the measuring
system to the external shield may take place, and may therefore have to be rather ex-
tensive. The effectiveness of any part of it can be told by disconnecting that part,
and noting the resulting effect on the deflection which is produced by connecting a
battery cell between measuring system and external shield at the furnace. The useful-

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[1] An arrangement apparently first used by C. N. Fenner, of this laboratory.

[2] Even if there were no connection to the shield at B, the leak from A to B would
still be balanced at the galvanometer by one from A' to B. This is probably the reason
why leaks wholly within the furnace are seldom noticeable in ordinary thermoelectric
measurements.

ness of this type of internal shield is probably limited to cases where an electric furnace is used.

Internal Battery Shield.

For thermoelectrical work, and in some similar cases, not specially considered here, a different form of *internal shield* is to be recommended, namely, one which diminishes leakages due to the potentiometer battery (or Wheatstone Bridge battery) itself. The ability to gain an advantage through this type of shielding arises from the very low voltage of the thermoelectric reading. This seldom reaches 0.02 volt, hence the potentiometer might be operated by a battery of 0.02 volt electromotive force, which, as far as leakage alone is concerned, would be more advantageous than the present custom. By shielding against most of the battery' voltage the leakage can be made no greater than is due to 0.02 volt or less, while the other advantages of an ordinary battery are retained. Of course the leakage with an unshielded 2-volt battery will be considerably less than that coming from the fifty volts or more which often occurs externally. Nevertheless, the battery leakage may evidently be appreciable if the insulation resistance at any one of several points falls much below 100,-000,000 ohms; and the battery shield, like other shields, costs very little trouble to instal and none to maintain. It is, therefore, at any rate a method of simplifying matters by eliminating absolutely one possible source of error.

The battery shield is precisely analogous to the external shield as used in power measurements. It shields the whole gavanometer circuit from the rest of the battery circuit and it is kept at the same potential as the galvanometer circuit by a connection to the battery circuit near the galvanometer circuit. It therefore must effect an "electrical" separation (in the sense defined in the second foot-note to this paper) between the galvanometer circuit, on the one hand, and the battery, with other associated apparatus, on the other. A metal plate under the battery and associated apparatus, or something equivalent, is all that is needed.[1] The plate need not extend under the rest of the galvanometer system. The connection from circuit to shield can be made through the potentiometer (battery) terminal nearest in potential to those potentiometer coils which may lie in the galvanometer circuit, that is, through the terminal nearest in potential to the zero points of the potentiometer dials.[2]

[1] The necessary conditions are also met, in the case of the battery, if that is suspended by a wire connected to the plate—a very convenient arrangement in many cases. Of course the upper end of the wire should be suitably insulated from other apparatus.

[2] A connection made to a point between the galvanometer circuit coils and the coil used to balance the standard cell causes the same sort of error as a connection to K in Fig. 3. In general, this cannot happen if the connection is to the potentiometer terminal nearest the zero, but it may occur, if not guarded against, whenever the standard cell coil is in a separate box.

Since the battery-shield is connected to the measuring system it must be insulated from the external shield, unless the system is sure to be insulated from the external shield at every other point.

In a combination potentiometer, each battery circuit should be shielded.

Surface Shielding.

Further extensions of the battery shield are often desirable, and are made easy by a different method of arranging the shield, which is admissible in many cases. It has already been seen that wherever insulation is effective shielding is unnecessary, and that this principle is applicable to the air, which (usually) is the seat of no leakage. The same thing is true of the *interior* of blocks of hard rubber, porcelain, etc. All the leakage that goes by these passes over their surfaces. With them, therefore, shielding is quite complete which intercepts all the surface leakage, and this may be very easily and effectually done by simply pasting strips of tinfoil on the surface, connecting these, if necessary, to the other parts of the shield.

The Battery Shield and the Eliminating Switch.

In making the adjustment or eliminating parasitic E. M. F.'s[1] from the galvanometer circuit, the usual treatment of the battery current has been either simply to interrupt it, or, with potentiometers of lower resistance, where interruption would impair the constancy of the voltage, to switch the current through another resistance equal to the potentiometer. In either case there will sometimes be, between different parts of the switch, potential differences equal to the whole battery voltage. It will then be necessary, if the insulation cannot be thoroughly relied on, first, to bring the battery shield into the switch, by surface shielding or otherwise, in such a way that when the switch is open the two or three terminals with their leads shall be completely shielded from each other, and second to put the switch at the opposite end of the potentiometer from the shield connection, since it is evident that a shield connected at the same end cannot prevent the leakage current through the open switch from traversing the potentiometer.

The necessity for shielding in the switch is, of course, avoided by the newer arrangement described in connection with Fig. 7 of the previous paper on potentiometers,[2] where the negative terminal of the battery is merely shifted from the negative potentiometer terminal to a point just beyond the galvanometer circuit coils so as to eliminate these coils, and these only, from the battery circuit. All parts of the switch then remain at nearly the same potential. The substitute resistance is also usually avoided, though if the slight change of current due to the side-tracking of

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[1] As described in the first paper of this series, Sec. 5; THIS JOURNAL, **36**, 1859 (1914).

[2] THIS JOURNAL, **36**, 1876 (1914).

the few coils should make the battery a little inconstant, a *small* substitute resistance can be put in series with the extra terminal. With this arrangement the switch must come between the potentiometer terminal and the connection to the shield, for in that way only is the necessary direct connection of shield to battery circuit preserved. Otherwise, when the intermediate terminal is in use the shield is connected to the battery circuit through the eliminated coils, which are therefore traversed by any leakage current which may be returning by way of the shield.

Leakage on the Potentiometer Top.

A hard rubber potentiometer top, if not carefully shielded from light, may easily become, in the course of a few years, the leakiest part of the measuring system. This trouble, however, can usually be corrected without difficulty. (1) In low range potentiometers, shielding upon the potentiometer top is easy, for (a) the leakage is confined to the external surface, so that tinfoil strips are adequate, and (b) the positive terminals of the potentiometer and of the standard cell coil are the only points far from the negative terminal in potential and therefore the only points to be shielded.

(2) The leaky condition of the hard rubber can also be directly removed by warming the top in one place after another with the radiation from an incandescent light, and then applying melted paraffin. This cure is not permanent, at least not on rubber that has once been leaky, such a treatment has twice needed repetition in the course of three years. The operation, however, is not long nor difficult. A very effective control of leakage by means of it could hardly be called laborious.

Good results in leakage prevention are also reported for the method of occasionally wiping the hard rubber surfaces with dilute ammonia.

In case a new instrument is to be set up it might often be well to cover it with a light-proof case, through the top of which pass rods for operating the switches. The same end is readily attained with a glass-topped potentiometer,[1] by simply laying a black cloth on the glass.

Final Considerations.

In the thermoelectric system described in this and other papers of the present series, leakage has proved to be—barring, of course, accidents and outright mistakes—the only considerable source of unexpected errors. The methods of leakage prevention here described, therefore, increase greatly the certainty and reliability of the system, and, being very simple and easy to instal, are to be recommended. Such of them as have to do with the insulating quality of surfaces need, of course, to be tested, but the tests are not difficult and need not be made often Battery and other electrolytic leakage is not much affected by the position of the poten-

[1] Walter P. White, *Instrumentenkunde*, **34**, 79 (1914).

tiometer switches;[1] hence, it can be tested for by connecting the external line directly to the external shield, setting the switches on zero, and then noticing if any change of deflection occurs on connecting or disconnecting the battery. The connection to the external shield in this test may be omitted if it is certain that the insulation between that and the measuring system will be as good in later work as it is at the time of the test.

The effectiveness of the external shield is certain if the shield is complete and is intact. Furnace leakage through an incomplete shield can be detected by reversing the furnace current, and the resulting false deflection (usually) can be measured by interrupting it.

Summary.

1. An insulation resistance of 5,000 megohms or more is often necessary to prevent serious disturbance of thermoelectric measuring systems from stray portions of power or lighting currents, and the frequently more sensitive resistance measuring system is of course in greater danger still. All such trouble is absolutely prevented by an equipotential shield, which is merely a connected system of metal plates, wires, etc., which interposes itself at every point of solid contact between the measuring system and external bodies. This shield need not be, and preferably should not be, "earthed."

2. Slight modifications of this shield are also useful in electric furnaces, in measurements upon power circuits, and within the potentiometer circuit itself.

3. These arrangements are easy to instal; most of them require no subsequent attention, and all are easily tested.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

THE VAPOR PRESSURES OF SILVER, GOLD AND BISMUTH AMALGAMS.
BY ERMON DWIGHT EASTMAN AND JOEL H. HILDEBRAND.

The measurements presented in this paper on the vapor pressure of amalgams of silver, gold and bismuth are a continuation of an extensive study, planned and begun by one of us, of the laws of concentrated solutions from the standpoint of metallic solutions. Measurements on the vapor pressures of zinc amalgams have already been published,[2] and measurements by others of the electromotive force of amalgam concen-

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[1] This statement is here intended to apply only to the case of thermoelectric work, where the maximum change of switch setting is only a few millivolts.

[2] Joel H. Hildebrand, *Orig. Com. 8th Internat. Congr. Appl. Chem.*, **22**, 147; *Trans. Am. Electrochem. Soc.*, **22**, 319 (1912).

tration cells have been considered,[1] along with the vapor pressure measurements, in the light of Raoult's law, taking account, following Dolezalek,[2] of chemical changes such as solvation and association. For the progress of the work up to this point, as well as references to the literature on the subject, we would refer the reader to the previous papers.

Experimental Method.

The procedure followed has been essentially that used in the measurements on zinc amalgams. The amalgams whose vapor pressures were to be measured were confined in U tubes of the type shown in Fig. 1, in volumes a little more than sufficient to fill the closed limb of the tubes. The tubes were filled by introducing mercury and the metal in the desired proportions, the amalgamation and mixing being accomplished by the subsequent heating and vigorous agitation of boiling out. The angles in the tubes prevented portions of amalgam being carried over by the vapor during the boiling out. For the oxidizable bismuth amalgams, tubes like that of Fig. 2 were used. In this case the amalgams were formed by heating known weights of the constituents in the arm a, in an atmosphere of hydrogen. When the amalgams were run through the capillary b, into the U, all dross remained behind. The tubes were then sealed off at b. Hydrogen being now the gas in the tubes and apparatus, there was no oxidation.

When filled, the tubes were placed in the thermostat, connected to a mercury manometer

Fig. 1.   Fig. 2.

as shown in Fig. 3, and boiled out under reduced pressure to eliminate gas in the closed arms. Pressure in the open arm, sufficient to balance the pressure of mercury vapor in the closed arm, as indicated by the coincidence of the levels of the amalgam menisci, was then restored. After allowing time for thermal balance to be obtained, finer adjustments of pressure were made by means of the mercury reservoir shown, and the pressures read on the manometer. The relative pressure of solution and solvent being the quantity sought, a tube containing pure
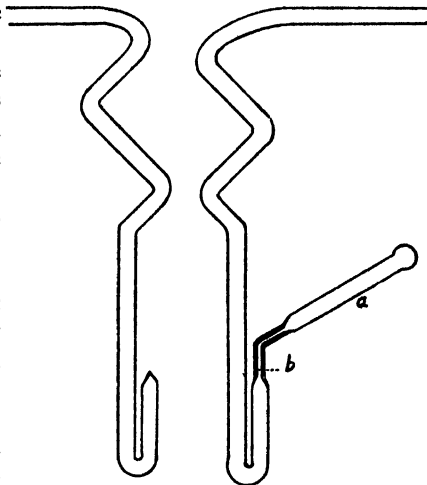
[1] *Orig. Com. 8th Internat. Congr. Appl. Chem.*, **22**, 139; *Trans. Am. Electrochem. Soc.*, **22**, 335 (1912)

[2] *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910).

mercury was connected to a separate manometer of the same type, and observations made upon it immediately following and under the same conditions as the amalgam determinations. From these measurements, also, the temperature was given by the careful measurements of Smith and Menzies[1] on the vapor pressures of mercury.

The thermostat consisted of a tall beaker resting in a similar beaker one size larger, which served as a jacket. Fused sodium and potassium

To Manometer
for Pure
Mercury Tubes.

To Pump.

H₂
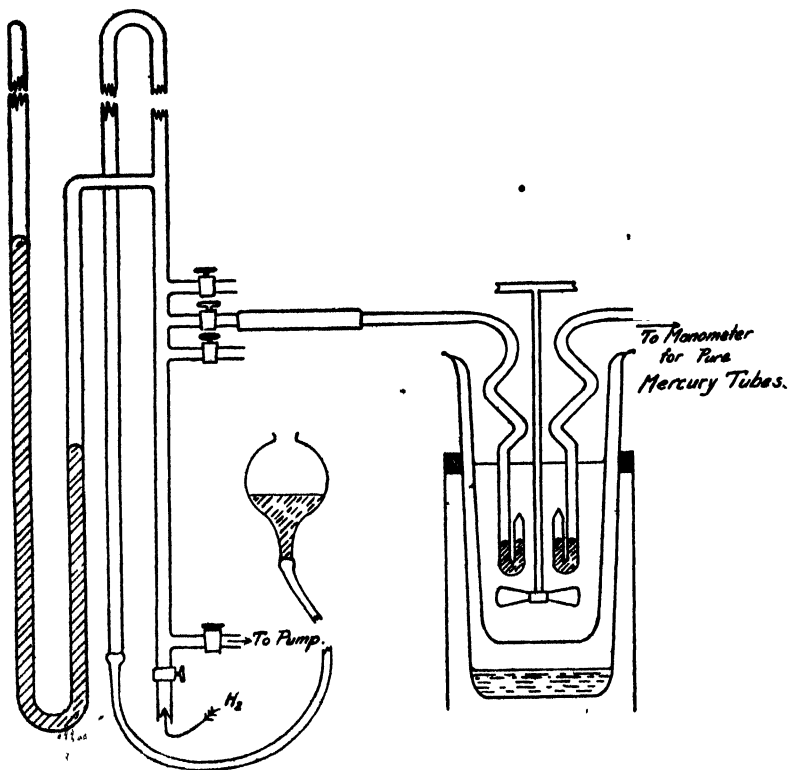
Fig. 3.

nitrate mixture, vigorously stirred, furnished the bath for the tubes, heated by the vapor of boiling phenanthrene in the outer beaker. The outer beaker was protected to the level of the inner bath by a glass cylinder cut from another beaker. The exposed portion acted as a condenser for the phenanthrene vapors. A Méker burner was the source of heat. In starting the thermostat, the nitrates were fused separately and poured into the inner beaker, which was already heated by the boiling phenan-

[1] THIS JOURNAL, 32, 1434 (1910).

threne. At the conclusion of a run both the nitrates and the phenanthrene were removed from the beakers. During observations the top of the thermostat was covered as well as possible with strips of mica. The constancy of temperature attainable may be seen in the tables of results.

Sources of Error.

The quantities to be determined were the relative vapor pressures and the atomic fractions of the amalgam constituents at constant temperatures.

The variation of relative pressure with the temperature is not large. The practically simultaneous determination of the pressures from amalgam and mercury, therefore, eliminate the observed variations in the temperature as serious sources of error, provided equilibrium was reached.

The error due to impurities in the materials would appear in the estimation of the atomic fraction. The mercury used was carefully purified by washing in dilute nitric acid[1] and distilling in a current of air.[2] The gold and silver were also purified in the laboratory by the usual methods. Kahlbaum's bismuth was used. Since there are no abnormally large effects due to traces of impurities, the error from this source was negligible. There were slight variations from the values of the concentrations, as had from the weights of the constituents, on account of the condensation of small amounts of mercury in the upper portions of the tubes. This, too, was negligible, except in the case of the extremely concentrated bismuth amalgams. Here a correction was made by weighing the condensed mercury. It was, of course, always possible, though seldom necessary, to analyze the amalgams after the experiment, if any doubt as to its composition existed.

The accuracy of the results was determined, it is seen, by the accuracy of the pressure determinations. This was preserved, as far as possible, by the elimination, by boiling out, of the gas which it was found was given off by the glass in varying amounts in the closed arm during determinations. Condensation of the vapor of mercury in the closed arm by increasing the pressure permitted very small amounts of gas to be detected at the point of the tube. The tubing was of large enough diameter to minimize any unequal effects of surface tension in the different arms of the tubes. An incandescent bulb placed behind the thermostat enabled the menisci to be easily observed. The error in adjustment and reading of the pressures, it is estimated, was not greater than a millimeter. This was greatly reduced by making a number of observations for each determination. The degree of agreement of these separate observations among themselves can be seen from the tabulated results. Due, probably, to increasing skill in manipulation, this was markedly better in the case of bismuth than of gold.

[1] Hildebrand, THIS JOURNAL, 31, 933 (1909).
[2] Hulett, *Phys. Rev.*, 33, 307.

Experimental Results.

Silver Amalgam.—In Table I are given the results upon the vapor pressure of the single silver amalgam investigated. From a preliminary series of measurements it was found that silver is but slightly soluble in

TABLE I.—SILVER AMALGAM.

	P.	P_0.	P/P_0.	t.
Wt. Ag 0.1783	318.2	325.3	0.978	313.1
Wt. Hg 14.013	318.2	325.7	0.977	313.2
N = 42.27	318.4	325.7	0.977	313.2
	315.4	324.7	0.972	313.0
	317.7	324.7	0.979	313.0
	318.1	325.7	0.977	313.1
		Mean,	0.9767	313.1
		$N/N+1$	0.9769	

mercury, even at these temperatures. On that account but one accurate determination was made. In the table, P denotes the vapor pressure of the amalgam, P_0 that of mercury at the same temperature, t the corresponding temperature, according to the measurements of Smith and Menzies,[1] and N the number of atoms of mercury per atom of solute metal.

Gold Amalgams.—In order to save space we give the individual observations on but one amalgam, as a sample, in Table II. The results of the other series of observations are merely summarized in Table III, including the "probable error" of each set of observations of P/P_0, cal-

TABLE II.—GOLD AMALGAM.

	P.	P_0.	P/P_0.	t.
Expt. No. 27	344.9	350.1	0.986	316.7
Wt. Au 0.2018 g.	346.5	353.3	0.982	316.1
Wt. Hg 13.328 g.	345.3	351.5	0.983	316 7
N = 65.0	348.0	352.9	0.990	317.1
$N/N+1$ = 0.985	351.5	355.2	0.990	317.4
	351.5	356.1	0.988	317.6
	351.0	355 5	0.988	317.4
	351.9	356.3	0.988	317.6
	351.3	356.5	0.987	317.4
	352.0	356.1	0.988	317.4
	352 7	356.1	0.991	317.4
		Mean,	0.987	317.3

culated by the usual formula. These results are represented graphically in Fig. 4, relative pressures, P/P_0, being plotted against the atomic fractions of gold, $1/N + 1$.

Bismuth Amalgams.—Here again we will not burden the text with an extended series of tables of the separate series of observations, but summar-

[1] *Loc. cit.*

TABLE III.—GOLD AMALGAMS.

Wt Au	Wt Hg	No of obs	N	$1/N + 1$	P/P_0	"Prob error" ±	t.
0 2018	13 328	11	65 0	0 0152	0 987	0 0006	317 3
0 5707	14 002	14	24 1	0 0398	0 979	0 0005	316 6
0 7436	12 541	13	18 14	0 0652	0 968	0 0006	315 4
0 997	13 125	10	12 96	0 0717	0 955	0 0006	317 5
1 269	12 666	8	9 84	0 0925	0 950	0 0014	313 0
1 354	11 796	6	8 81	0 1046	0 945	0 0005	319 8
1 636	12 441	12	7 48	0 1179	0 942	0 0006	317 5
2 363	13 125	3	5 56	0 153	0 931	0 0013	315 9
109	13 125	2	4 22	0 191	0 933	0 0013	316 2

are the mean values, giving the calculated "probable error" of the observed ratios P/P_0. The summary is given in Table IV. The results are plotted in Fig. 4, the ordinates, as before, being the relative pressures P/P_0 and the abscissae the atomic fractions of bismuth $1/N + 1$.

TABLE IV —BISMUTH AMALGAMS

Wt Bi	Wt Hg	No of obs	N	$1/N + 1$	P/P_0	"Prob error" ±	t	P/P_0 calc	Difference.
0 4125	7 388	5	18 57	0 0510	0 961	0 0007	320 3	0 960	+0 001
1 504	10 690	4	8 31	0 1074	0 929	0 0004	320 3	0 927	+0 002
2 647	14 644	4	5 73	0 1486	0 908	0 0002	321 1	0 904	+0 004
3 669	10 757	4	3 05	0 247	0 840	0 0004	321 0	0 8	—0 002
7 865	14 274	3	1 88	0 347	0 765	0 0006	320 9	0 765	±0 000
7 582	8 485	4	1 16	0 463	0 650	0 0005	320 3	0 658	—0 008
11 201	8 383	5	0 777	0 563	0 542	0 0007	321 9	0 552	—0 010
12 576	6 334	5	0 522	0 670	0 432	0 0007	320 3	0 428	+0 004
19 598	4 980	4	0 262	0 793	0 278	0 0004	321 7	0 277	+0 001
9 328	0 618	2	0 0686	0 937	0 092	0 002	321 2	0 088	+0 004

Interpretation of the Results.

The expression most frequently used for calculating vapor pressures of binary mixtures is Raoult's law,

$$P/P_0 = N/N + 1.$$

It will be seen that the dilute silver amalgam investigated obeyed this law very closely, as all solutions undoubtedly would if sufficiently dilute. At this concentration, therefore, we may regard the atom and molecule of silver as identical, confirming the results of Ramsay.[1]

Turning next to bismuth amalgams, we see from Fig 4 that the relative vapor pressures are greater than those calculated from the simple Raoult law, which would give a straight line, as indicated   There are two methods whereby such deviations have been accounted for.   The first is to assume that Raoult's law is fundamentally correct, and that all apparent deviations are due to a change in the real mol-fraction, caused by a change in the molecular species present.   For example, if the bismuth were completely associated to form Bi_4, then there would be not 1 mol of bismuth to N of

[1] *J. Chem Soc*, **55**, 521 (1889).

mercury, but 0.5 mol, and the relative vapor pressure of the mercury would be given by the equation,

$$P/P_0 = N/N + 0.5.$$

Such a modification of Raoult's law gives values of P/P_0 for bismuth
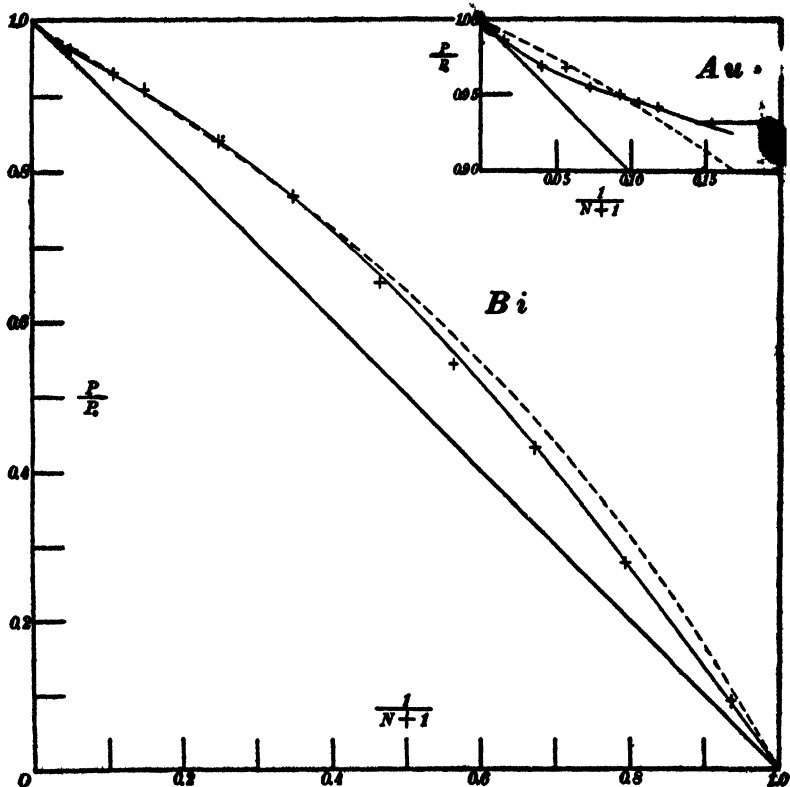
Fig 4

amalgams which are too great. The next step would be to assume a partial association according to the equation

$$2Bi \rightleftharpoons Bi_2.$$

Here, if α represents the mols of Bi_2 formed, and $1 - 2\alpha$ the mols of Bi present, then we would have for the mol-fraction of mercury

$$P/P_0 = N/N + 1 - \alpha, \qquad (1)$$

α and N being connected with the equilibrium constant K of the above equilibrium by the equation

$$K(1-2\alpha)^2/(N+1-\alpha)^2 = \alpha/(N+1-\alpha)$$

or
$$K(1-2\alpha)^2 = \alpha(N+1-\alpha) \tag{2}$$

The elimination of α between Equations 1 and 2 gives the formula used successfully to calculate the relative vapor pressures of zinc amalgams[1] and the e. m. f. of concentration cells of zinc, lead and tin amalgams.[1] In the present case, however, we find that the observations will not fit this type of curve. If $K = 40$, P/P_0 is given by the broken curve in Fig. 4. It will be seen that the relative pressures are given fairly well up to a bismuth concentration of about 33 atom-per cent., but for more concentrated amalgams the observed values lie considerably below the curve. Nor is it possible to improve the agreement by altering the value of K. A smaller value of K would reduce the calculated values of P/P_0 chiefly at the left end of the curve in the figure, rather than at the right, where $1/N + 1$ is large. The discrepancy could undoubtedly be removed by assuming a second equilibrium whereby there is partial formation of Bi_2Hg. This would introduce a second equilibrium constant into the equation for P/P_0, and give a very complicated expression, in spite of the fact that it would contain but two constants. The method for doing this is obvious, and it hardly deserves the space that it would require.

The second method for calculating such curves is in accordance with the theory published in an important paper by van Laar.[2] As has been pointed out by Washburn,[3] the law of Raoult cannot hold where two liquids are present which are not completely miscible. The vapor pressure of either component must be the same from each liquid phase, while by no assumption can its mol-fraction be the same in both. In other words, the escaping tendency of one component from the phase composed largely of the other is greater than its mol-fraction in that phase, due, we may imagine, to the inability of molecules of the first component, having a volume b, to penetrate as easily a liquid composed largely of molecules of the second, having a different volume, b'.[4] Now, if such a system were subjected to a change of temperature so that the two liquid phases became one, we can hardly imagine that Raoult's law would suddenly become valid, since the cause of the deviation when two liquids were present has been gradually diminished rather than suddenly removed. The idea underlying van Laar's treatment of the question is, therefore, undoubtedly correct, as he introduces the values of b, in the sense of the van der Waals equation, and also a factor, β, depending on the heat of mixing. Refer-

[1] J. H. Hildebrand, *l. c.*
[2] *Z. physik. Chem.*, **72**, 723 (1910); **82**, 599 (1913).
[3] *Trans. Am. Electrochem. Soc.*, **22**, 330 (1912).
[4] The influence determining this difference between the relative escaping tendency and the mol-fraction have been termed by Washburn the "thermodynamic environment." In view of the kinetic explanation one is led to feel that the adjective might be omitted without any real sacrifice of meaning.

ence must be made to the original paper for the derivation of his equations and their theoretical consideration. We will merely give the equations there derived for each component.

$$P/P_0 = xe\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}, \quad \text{and} \quad P'/P_0' = (1-x)e^{-\frac{\beta x^2}{(1+rx)^2}}$$

where

$$r = (b-b')/b', \text{ and } x = N/N+1.$$

In our notation the vapor pressure of mercury from amalgams may be expressed in the simplified form

$$P/P_0 = Ny/N+1$$

where $\log_{10} y = a/(1+cN)^2$. By making approximate solutions it was found that the measurements are given very closely by this formula when $a = 0.1425$ and $c = 0.234$. The curve corresponding to these values is drawn in the figure, the calculated values of P/P_0 corresponding to the measured values are given in the 9th column of Table IV, and the differences between the calculated and measured values are seen in the last column. The agreement is seen to be quite satisfactory. The values of a and c here used are quite empirical. Data upon the heat of mixing are not at hand, so that the value of a cannot be tested. However, c depends upon the ratio of b for mercury to that for bismuth. This would probably be not very different from the ratio of the molecular volumes at these temperatures, which is approximately 0.75. This would give to r the value —0.25, and to c, 0.75. This is quite different from the empirical value given above, so that the equation expressing the observations should hardly be considered, at least for the present, as having any theoretical significance.

The values of P/P_0 for gold amalgams, as will be seen from the curve, deviate strongly from the simple form of Raoult's law as the concentration increases. The small solubility of gold in mercury at this temperature prevents any considerable portion of the curve from being realized experimentally. The appearance of a solid phase at a concentration of about 15 atom-per cent. is evident from the curve, and was obvious during the experiment. The deviations are too great to be accounted for by the assumption of the presence of the compound Au_3Hg, the existence of which is reported by G. McP. Smith[1] from evidence gained by diffusion experiments.[•] According to this assumption we should have

$$P/P_0 = (N-0.5)/N$$

The graph of this equation is given in the figure, and it is obvious that the measurements could be accounted for only by assuming a molecule containing more gold atoms and dissociating rather completely in dilute

[1] THIS JOURNAL, 36, 847 (1914).

solution to give Au molecules. The construction of a curve on the basis of such assumptions would have very little theoretical justification, in view of the small range of concentration over which it might be tested. Turning to the equation in the form given by van Laar, we find that a satisfactory agreement with the observed values is obtained by taking

$$\log y = 0.23/(1 + 0.25N)^2$$

The curve drawn through the points is calculated from these constants in the equation

$$P/P_0 = Ny/N + 1$$

These two methods of accounting for vapor pressures of mixtures seem to be very different, and they have been the subject of some harsh polemic between van Laar[1] and Dolezalek.[2] It would seem that neither point of view should prevail to the exclusion of the other. Undoubtedly there exist cases where chemical changes should be regarded as the chief modifying factor, and the treatment used by Dolezalek is substantially correct. It is equally certain, however, that all deviations from the simple law cannot correctly be accounted for in this way, and that curves, as drawn in Fig. 4, may be strongly convex upwards where no essentially chemical changes are involved, and where the general principle underlying van Laar's treatment of the problem must be invoked. Some external evidence must be sought in many cases to decide in how far individual deviations from the simple law should be explained by one method or the other. For example, if we extrapolate from our measurements to find the condition of bismuth when $N = 0$, i. e., when pure liquid bismuth is present, we find that according to the method of van Laar it might be monatomic, in spite of the convexity of the curve in Fig. 4, whereas, according to the method maintained by Dolezalek, it must be more or less associated. Now if we should find independent evidence as to the molecular weight of molten bismuth, we would be in a position to lend strong support to one or the other of these two points of view. A study of such evidence is being made, and will be the subject of a communication in the near future. We hope, also, that further light will be shed upon the subject by the vapor pressure measurements planned upon other amalgams. For the present, therefore, we will forego further discussion, and rest with the presentation of the above facts.

Summary.

Measurements have been made of the vapor pressures of silver, gold and bismuth amalgams, at approximately $318°$. Silver being but slightly soluble at this temperature, one measurement only was made, with an

[1] L. c.
[2] Z. physik. Chem., 83, 40 (1913).

amalgam containing 1.27% of silver. Raoult's law was found to be obeyed within the limit of experimental error.

Measurements with gold amalgams at concentrations up to 23.7% of gold showed the separation of a solid phase at an approximate composition of 16.5%. In the more dilute amalgams the vapor pressures were found to be greater than those calculated from the simple form of Raoult's law. The deviation is such that to explain it on the basis of Raoult's law one would have to assume a rather complex gold molecule. The observations are very well expressed by the equation:

$$\frac{P}{P_0} = \frac{N}{N+1}\; 10^{\frac{0\,23}{(1+0\,25\,N)^2}}$$

This equation corresponds in form to one derived by van Laar, but with values assigned to the constants which are purely empirical.

Bismuth amalgams of all concentrations are liquid at this temperature, and, like gold amalgams, gave vapor pressures higher than those calculated from Raoult's law. If the validity of that law is assumed the deviations from its simple form could be explained by assuming the two equilibria:

$$2Bi \rightleftharpoons Bi_2, \text{ and } Bi_2 + Hg \rightleftharpoons Bi_2Hg$$

This would give an equation containing but two constants, but complicated in form. The equation of van Laar, which permits deviations from Raoult's law without assuming association or other chemical changes, again expresses the observations very accurately when numerical values are chosen as follows:

$$\frac{P}{P} = \frac{N}{N+1}\; 10^{\frac{0.1425}{(1+0.234\,N)^2}}$$

It is pointed out, however, that too much stress should not be placed upon this agreement on account of the entirely empirical nature of the constants assumed.

To decide to what extent deviations from the simple Raoult's law should be accounted for by either of the two methods, it is shown that recourse must be had to other methods for distinguishing between normal and associated liquids.

BERKELEY, CAL.

THE MEASUREMENT OF OXIDATION POTENTIALS AT MERCURY ELECTRODES. I. THE STANNIC-STANNOUS POTENTIAL.

BY GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

The existing data on oxidation potentials are neither so abundant nor so concordant as the importance of the subject would warrant. This remains true of the stannic-stannous potential, for instance, in spite of

careful investigations by Bancroft,[1] Fredenhagen,[2] Dolch,[3] and Foerster and Yamasaki.[4] Thus, Fredenhagen, working in solutions tenth-normal with respect to both hydrochloric acid and tin, the stannic concentration being twenty-four times the stannous, noted potentials varying two-tenths of a volt, and not approaching constant or agreeing values after days of waiting. Dolch, working in several concentrations of sodium hydroxide, fared better, but did not record enough results to draw sweeping conclusions as to the reproducibility of his figures, or the effect of the variable concentrations. Yamasaki gives seven determinations, three with pink salt, three with half-normal acid, and one with twice normal acid where the concentration ratio of the tin salts is not recorded. Both of the last-mentioned investigators waited from five to twenty days before sufficient constancy was attained to justify recording measurements.

It appeared that improvement would be impossible if platinum electrodes were used as in the above researches. Fredenhagen has pointed out the difficulties arising from solutions which do not react readily with oxygen, and which thus fail to come into equilibrium with the hypothetical platinum oxides which are supposed to carry over the potential to the platinum itself.

Of other electrode materials, gold and palladium were tried by Peters.[5] Abegg[6] was probably the first to suggest the use of base metals, especially copper, though he did not publish any results. Mazzucchelli,[7] in his research on the chromic-chromous potential, used copper, silver, and mercury. His difficulties, as will be shown in a paper shortly to be published, lay in the decomposition of his solutions rather than in his electrodes, at least where mercury was used. This metal possesses the great advantages of a free surface on which hydrogen has a high overvoltage. Hydrogen undoubtedly deposits on platinum immersed in powerful reducing agents, and we have found that the potentials of such solutions are much more electronegative on mercury than on platinum, a strong point in favor of mercury electrodes. The effects of air on the two electrodes were studied in a stannic-stannous cell of the type described below, but provided with a platinum as well as a mercury electrode. This was brought to equilibrium as pure carbon dioxide, then air was passed in for a time, then carbon dioxide again. The single-potentials were recorded as follows:

[1] *Z. physik. Chem.*, 10, 399 (1892).
[2] *Z. anorg. Chem.*, 29, 443 (1902).
[3] *Z. Elektrochem.*, 16, 602 (1910).
[4] *Ibid.*, 17, 361 (1911).
[5] *Z. physik. Chem.*, 26, 198 (1898).
[6] *Z. Elektrochem.*, 13, 34 (1907).
[7] *Zentralblatt*, 76, II, 294 (1905).

Conditions.	Time. Min.	Mercury. Volt.	Platinum. Volt.
Equilibrium, CO_2	0	0.411	0.488
Air passed in	3	0.465	0.541
Air passed in	29	0.449	0.542
Air passed in	66	0.453	0.546
Air off, CO_2 on	74	0.424	0.520
Air off, CO_2 on	155	0.408	0.461
Air off, CO_2 on	234	0.409	0.474

The air evidently disturbs the potential on the platinum much more than on the mercury, and its effects are almost impossible to eliminate from the platinum, while the mercury quickly recovers. Hydrogen, on the other hand, was proved in a similar experiment to have very little effect on the potential at mercury electrodes.

The assumption is made, and verified below, that when constant potential is attained the oxidizing potential of the extremely dilute mixture of mercury salts present is equal to that of the stannic-stannous solution.

The single potential difference between mercury and its normal salts, 1.07 volts, sets a limit to its use in the study of oxidizing solutions. Solutions approaching this degree of oxidizing power would have to contain sufficient mercury salts at the start to avoid oxidation of metallic mercury, and as anion only perchlorate would be suitable. Perchlorate yields mercury salts freely soluble, and excess of the acid can be added to check hydrolysis without danger of oxidation due to the decomposition of the anion. In the presence of chloride, 0.56 volt, and in the presence of sulfate, 0.97 volt, the potentials of the corresponding standard electrodes, would be about the limits, if oxidation of mercury to insoluble salts is to be avoided.

Preparation of Materials and Solutions.—One-quarter of a gram atom of tin was dissolved in a known quantity of redistilled constant boiling hydrochloric acid in a flask provided with a ground-in reflux condenser terminating in a bent tube sealed with water to prevent entrance of air or escape of acid vapors. This water was added to the solution in the flask, and the whole made up to a liter, so that both the concentration of tin and of acid could be calculated. For a part of the work, reagent tin containing traces of carbon, but no iron, was used. For some of the determinations in twice normal hydrochloric acid (Solution 5) a sample was electrolyzed from an anode of this tin in a solution of stannous chloride made by dissolving another portion in acid. The agreement in potential noted upon plotting the results on the curves shows the equivalence of the two samples within one or two millivolts. Mercury, already quite pure, was passed repeatedly through a tower containing mercurous nitrate, and then distilled *in vacuo*. Carbon dioxide was freed from oxygen in Emmerling towers containing cuprous or chromous chloride, and in the later work on solutions twice normal in acid, as an additional precaution, the gas was dried with phosphorus pentoxide and passed through elec-

trically heated tubes containing copper gauze. It was in every case finally bubbled through a solution of essentially the same composition as that in the cell, to avoid concentration changes in the latter. Chlorine was prepared by the action of hydrochloric acid on potassium permanganate.

The Cells.—These were made from wide-mouthed bottles of 250 cc. capacity, closed with rubber stoppers pierced with five holes. Through these holes respectively, passed a glass tube with a sealed-in platinum wire to dip into the mercury on the bottom of the cells; a centrifugal stirrer; a tube for the delivery of carbon dioxide; a tube through which a pipet could be introduced; and a capillary emptying into an indifferent solution. This connecting liquid was saturated potassium chloride except in the case of part of the measurements with normal acid, where 24% of potassium nitrate was substituted for the same amount of chloride. The indifferent electrolyte was changed at frequent intervals.[1] It was connected by another capillary with the normal calomel electrode made up in a 125 cc. bottle, and checked at frequent intervals against a standard electrode carefully guarded from contamination. Connecting tubes gelatinized with agar agar were rejected as giving inconstant results. The whole system was immersed in a thermostat electrically regulated at 25.0°.

Both a potentiometer made by us from calibrated manganin resistance boxes and an elaborate Wolff potentiometer were used in making measurements. The compensation method was employed, a d'Arsonval galvanometer serving as a zero instrument, and several cadmium cells carefully made up serving as standards. Connections were carried in air lines or through glass tubes and other usual precautions observed. The cells, constantly swept out with pure carbon dioxide, were first filled with a solution of stannous chloride nearly free from stannic. After some hours the potential assumed a value which remained constant for days within 0.002 volt, provided no leakage of air or serious temperature change occurred. In the determination with Solution 1a, equilibrium was approached from the other side, by adding a trace of mercuric salt, which was reduced to mercurous salt and mercury until the oxidizing potential, due to mercury salts, was exactly equal to that of the stannic-stannous mixture. This conclusion, verified by the fact that these points also lie on the curve, demonstrates another point of superiority of mercury over platinum electrodes, where no corresponding experiment can be performed. All points on the curves were found with stationary though well mixed solutions, but figures noted on subsequent vigorous stirring are added in the tables.

Few workers in this field have taken the trouble to analyze their solu-

[1] A. C. Cumming and E. Gilchrist, *Trans. Faraday Soc.*, 9, 174 (1913), while urging the frequent formation of new boundaries, recommend that capillaries be not used at all.

tions after each potential measurement.   In the present research 10 cc. were always pipetted off into a flask swept out with carbon dioxide, diluted generously with air-free water, and titrated with 0.2 equivalent normal permanganate standardized at intervals with sodium oxalate from the
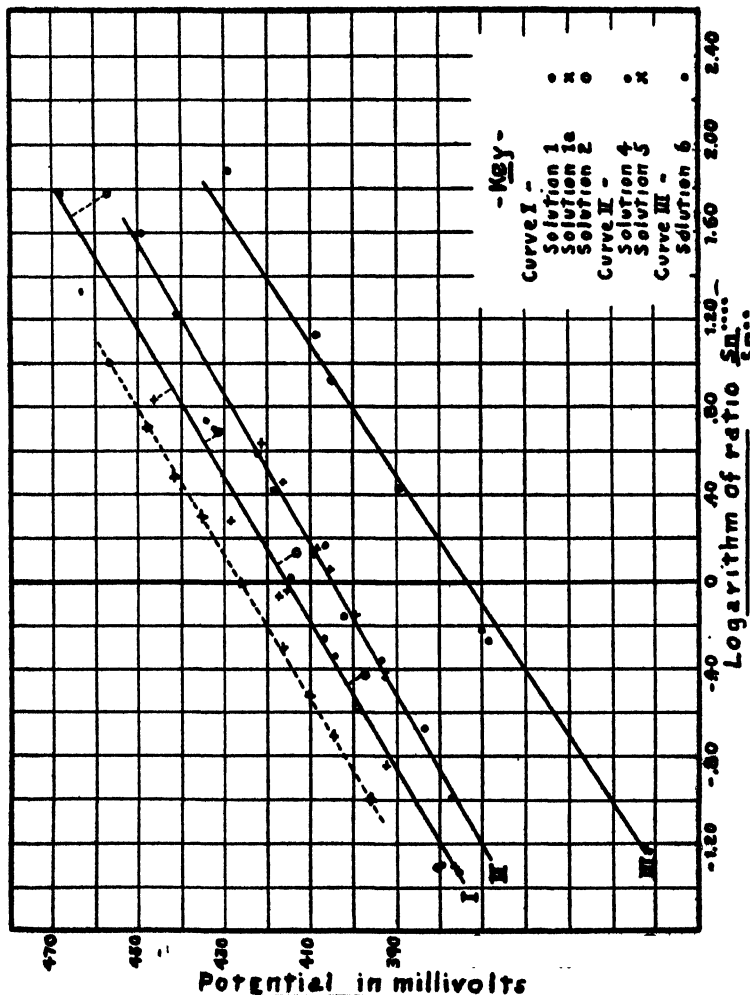
Fig. 1.

Bureau of Standards.   It was shown by adding iodide and starch that no chlorine is set-free previous to the last drop of permanganate, if only the solution is agitated.   The addition of ferric chloride[1] and manganous

[1] Olsen, "Quantitative Chemical Analysis," 1904, p. 312.

salts had no effect on the results, and these reagents were in general omitted.   End points were sharp and permanent.   The amount of stannous salt thus found was subtracted from the total tin to find the stannic content.   Next chlorine was passed in to change the concentration ratio, the acid concentration remaining constant, new measurements were then made, and so on until little stannous tin remained   As expected, the sharpest results were noted when neither valence was present in minimal concentration.

In the following tables each single potential as given results by subtracting the potential of the cell from the value assumed for the normal calomel electrode, namely o.560 volt.   This electrode always formed the positive pole of the cell.   The correction for the potential at the

TABLE I

Solution No 1

28 78 g tin per liter   1 016 N hydrochloric acid

Cell No	$\dfrac{Sn^{IV}}{Sn^{II}}$	$Log \dfrac{Sn^{IV}}{Sn^{II}}$	Time Hrs	π in millivolts	
				At rest	Stirring
2	0 0462	—1 34	92	375	376
1	0 0500	—1 30	92	379	383
1	0 4540	—0 34	48	404	405
2	0 5440	—0 26	48	406	406
1	1 035	0 01	20	414	414
1	5 008	0 70	23	432	432
2	5 435	0 74	20	434	434
2	60 15	1 78	24	468	

Solution No 1a

The same solution as in No 1, but each equilibrium was attained after addition of mercuric chloride

2	0 0485	—1 31	26	376	377
1	0 0504	—1 30	67	376	380
1	0 1444	—0 84	14	392	394
1	0 8600	—0 07	44	417	423
2	0 9145	—0 04	19	415	415
2	1 897	0 28	24	428	429
1	6 735	0 83	49	446	447

Solution No 2

29 69 g tin per liter   0 998 N hydrochloric acid

Cell No	$\dfrac{Sn^{IV}}{Sn^{II}}$	$Log \dfrac{Sn^{IV}}{Sn^{II}}$	Time Hrs	π	
				At rest	Stirring
2	0 0298	—1 52	89	374	379
1	0 0481	—1 31	89	380	385
1	0 2690	—0 57	23	399	399
2	0 3740	—0 42	23	397	398
2	1 390	0 14	21	413	414
1	4 860	0 69	21	431	436
2	60 90	1 78	21	457	462

Solution No. 4.

29.69 g. tin per liter.   2.000 N hydrochloric acid.

Cell No.	$\frac{Sn^{IV}}{Sn^{II}}$.	Log $\frac{Sn^{IV}}{Sn^{II}}$.	Tin Hrs.	At rest.	Stirring.
1	0.1033	—0.99	22	377	377
3	0.2118	—0.67	25	383	385
3	0.4420	—0.36	22	393	393
2	0.6879	—0.16	21	402	402
2	1.332	0.13	23	409	409
3	1.518	0.18	21	406	407
1	2.657	0.42	27	...	418
2	3.916	0.59	24	422	424
2	17.10	1.23	72	441	440
2	39.93	1.60	22	449	449

Solution No. 5.

Of same composition as solution No. 4, but prepared with electrolytic tin.

2	0.3651	—0.44	72	392	391
1	0.3900	—0.41	72	392	392
2	0.7014	—0.15	20	399	399
1	1.142	0.06	29	405	405
2	1.456	0.16	29	408	407
2	2.909	0 46	26	416	417
1	4.408	0.64	26	421	422

Solution No. 6.

29.69 g. tin per liter.   5.257 N hydrochloric acid.

Cell No.	$\frac{Sn^{IV}}{Sn^{II}}$.	Log $\frac{Sn^{IV}}{Sn^{II}}$.	Time. Hrs.	At rest.	Stirring.
1	0.0584	—1.23	86	331	...
2	0.0622	—1.21	95	332	331
3	0.1833	—0 90	28	342	343
2	0.5333	—0.27	23	368	368
1	0.6012	—0 22	19	371	372
3	2.622	0.43	42	390	391
2	8.479	0.93	21	405	406
1	13.41	1.13	21	408	409
1	77.76	1.89	23	427	429

liquid junction between the potassium chloride and the acid is not applied because of the great uncertainty as to the nature, concentration, and degree of dissociation of the numerous compounds and complex ions that may be present.   It will be shown that the best method to eliminate this uncertainty is to extrapolate to zero concentration of acid.   The data in the table are plotted on the lines found in Fig. 1.   Time elapsed, in hours, from the last alteration of concentration to the given observation is noted; in practically every case the potential was sensibly constant for the last twelve hours of this period.   The work in normal acid (Curve 1) was carried out first, before experimental difficulties had been thoroughly overcome, so that the points in this series are somewhat less satisfactory than in the others.

Unless considerable acid is present, the hydrolytic equilibrium of stannic chloride is very slowly established, as indicated by Kowalewsky's conductivity measurements,[1] which we checked at 25°. For each con-
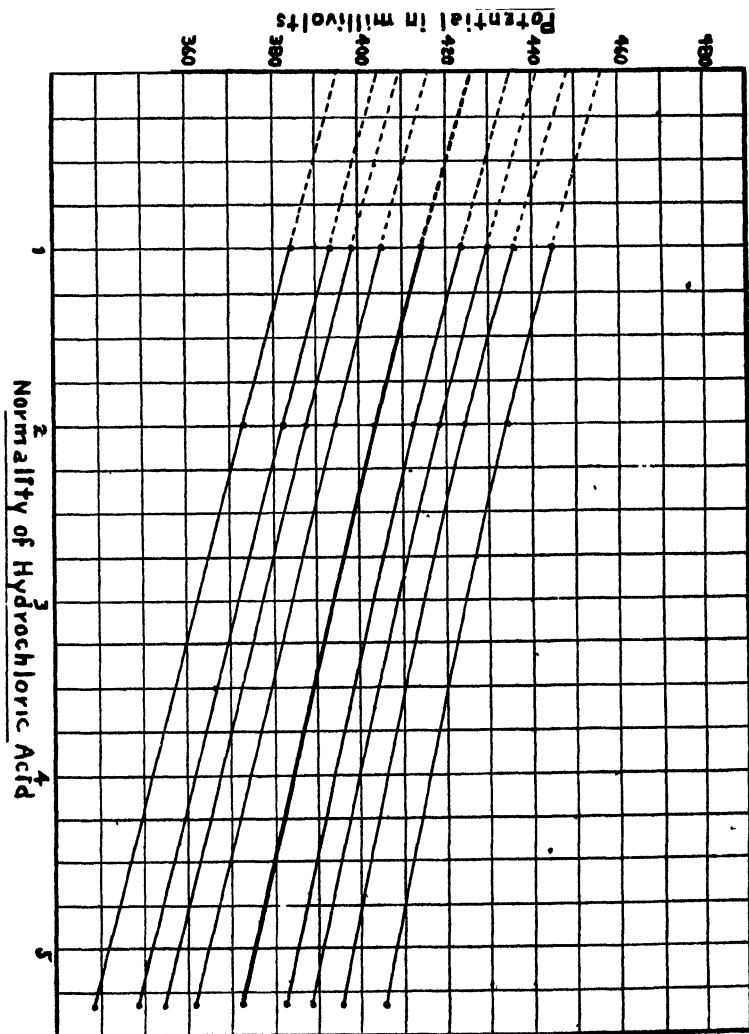
Fig. 2.

centration of acid used as a medium the curves show a relation, almost linear, between potential and the logarithm of the concentration ratio.

[1] *Z. anorg. Chem.*, **23**, 1 (1900).

To find what values ought to be observed if acid could be eliminated without appearance of hydrolysis, we have in Fig. 2 plotted potentials for selected values of the concentration ratio against the several concentrations of acid employed, and extrapolated to zero concentration of acid. Values taken from the smoothed curves are used in preference to experimental points, and are given in Table II.

TABLE II.

$\frac{Sn^{IV}}{Sn^{II}}$.	Log $\frac{Sn^{IV}}{Sn^{II}}$.	Potential in millivolts.		
		1 00 n.	2 00 n	5.26 n.
0 10	—1 00	385	374	339
0 20	—0 70	394	383	342
0 30	—0 52	399	388	355
0 50	—0 30	406	395	362
1 00	0 00	415	404	373
2 00	0 30	424	413	383
3 00	0 48	430	419	389
5 00	0 70	436	425	396
10 00	1 00	445	434	406

The graphs are nearly straight lines, so that no unusual risk is involved in the extrapolation to zero acid concentration. The dotted line in Fig. 1 shows these ideal stannic-stannous potentials, which can never be realized experimentally.

It is instructive to calculate the slopes of the several lines, considering the whole length in each case, and to compare them with the ideal slope of the line representing the equation $\pi = a + 0.029 \log \frac{Sn^{\cdots\cdot}}{Sn^{\cdot\cdot}}$, where $\frac{Sn^{\cdots\cdot}}{Sn^{\cdot\cdot}} = \frac{Sn^{IV}}{Sn^{II}} \cdot \frac{\alpha^{IV}}{\alpha^{II}}$. assuming $\frac{\alpha^{IV}}{\alpha^{II}}$, the ratio of the dissociation constants, to be invariable, a condition which is almost realized, apparently.

Concentration of HCl	0 n.	1.0 n.	2.0 n.	5.26 n.	Ideal.
Slope, $\Delta\pi/\Delta \log \frac{Sn^{IV}}{Sn^{II}}$	0 030	0 030	0.030	0.033	0.0295

Hydrochloric acid represses the ionization of stannic chloride and also of such complex ions as $SnCl_6''$ formed by the reaction

$$SnCl_4 + 2Cl' \rightleftarrows SnCl_6''$$
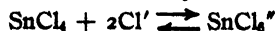
more than the ionization of the corresponding stannous compounds.[1] As there is no hydrolysis to check, increasing acid concentration causes $\frac{\alpha^{IV}}{\alpha^{II}}$, and, therefore, $\frac{Sn^{\cdots\cdot}}{Sn^{\cdot\cdot}}$, to fall off, which is demonstrated by the increasing slope obtained from the quotient $\Delta\pi/\Delta \log \frac{Sn^{IV}}{Sn^{II}}$.

[1] See Young, THIS JOURNAL, 23, 21 (1901), and Engel, Ann. chim. phys , 17, 338 (1889).

Effect of Varying Total Tin Concentration.—Cells were also observed containing but half the usual concentration of tin, that is, one-eighth of a gram-atom of tin per liter of normal hydrochloric acid.

TABLE III

Solution No 3

14 85 g tin per liter   o 999 N hydrochloric acid

Cell No	$\dfrac{Sn^{IV}}{Sn^{II}}$	Log $\dfrac{Sn^{IV}}{Sn^{II}}$	Time Hrs	π in millivolts At rest	Stirring
2	o 0487	—1 31	67	374	384
1	o 0668	—1 18	67	379	389
1	o 2865	—o 54	42	393	400
2	o 3560	—o 45	42	397	400
2	1 365	o 14	24	413	
1	2 375	o 38	24	427	
2	5 975	o 78	24	438	439

These values, if plotted as points in Fig. 1, would mingle with those found for twice this concentration of tin in normal acid. By subtracting from a number of potentials the quantity 0.029 log $\dfrac{Sn^{IV}}{Sn^{II}}$ all are reduced to a hypothetical condition where the concentration ratio equals unity.

Average

| 28 8 g per l ' | 415 | 414 | 417 | 419 | 416 | 420 | 414 | 415 |
| 14 4 g per l | 413 | 414 | 409 | 410 | 409 | 416 | 415 | 412 |

Thus it is shown that slightly more electronegative values result in the more dilute tin solution. Here the excess of chloride ions left free to repress the ionization of the stannic chloride and of its complexes is greater, and so the ratio $\dfrac{Sn^{IV}}{Sn^{\cdot\cdot}}$ is decreased. The difference, however, does not greatly exceed the limit of error of observation, and more exhaustive study would be necessary to settle the question even qualitatively, much more so quantitatively.

Until the degree of dissociation of the several stannic and stannous compounds involved, such as $SnCl_4$, $SnCl_6''$, H_2SnCl_6, $SnCl_2$, $SnCl_3'$, $HSnCl_3$, are known, it is impossible to unravel the various factors influencing the potentials. Were even a part of these known the above measurements would help to evaluate the rest. Meanwhile, mathematical treatment is altogether uncertain.

The work described in this paper was carried out in the spring of 1913, with the exception of the measurements in twice normal acid, which were made in the summer of 1914.

Summary.

Mercury is preferable to platinum in the measurement of oxidizing potentials of low intensity. Results are more quickly obtained, and

suffer less from irregularities in surface energy of the electrode and the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing one-quarter of a gram-atom of tin per liter in hydrochloric acid of three concentrations were measured at mercury electrodes at 25°. The probable error is about two millivolts.

Halving the total tin concentration makes the potential very slightly more electronegative; it seems to be nearly independent of the total tin concentration, other things being equal.

By extrapolation to zero concentration of acid, results are obtained which should be largely unaffected by uncertainties due to hydrolysis and to the single potential at the boundary between the cell liquid and the indifferent electrolyte.

Up to two moles of hydrochloric acid per liter, the potentials are quite accurately expressed by the formula

$$\pi = 0.426 + 0.030 \log \frac{Sn^{IV}}{Sn^{II}} - 0.011 \times \text{conc. HCl,}$$

provided sufficient acid is added to check hydrolysis.

Curves showing the relations existing among the several variables are discussed in the light of present knowledge of solutions of stannic and stannous chlorides.

CAMBRIDGE, MASS.

STUDIES ON A NEW KIND OF E. M. F.

BY REINHARD BEUTNER.

1. Introductory Remarks.

1. It was shown by the author[1] in previous communications that it is possible to compose galvanic cells of water-immiscible organic substances and aqueous solutions without metals, which, in certain points, exhibit properties like the well-known galvanic cells of which metals are the most essential component. The most important aim of a systematic study of these phenomena is the artificial reproduction and the explanation of the electrical properties of living tissues, since it is well known that these also produce e. m. f. resembling e. m. f. of metals. This fact was well established by electrophysiologists long ago, for the magnitude of the e. m. f. produced by tissues resembles that of ordinary galvanic cells; the same is found to hold for the cell-systems described here.

An experimental investigation undertaken at the suggestion of Dr. J. Loeb by the author[2] had shown this similarity of e. m. f. produced by

[1] THIS JOURNAL, 35, 344 (1913); Z. Elektrochem., 19, 467 (1913).
[2] Science, 34, 884 (1911); Biochem. Z., 41, 1 (1912).

tissues and metals in a still more striking form, for it was found that a quantitative law especially characteristic for metals (Nernst's formula) could be applied to tissues. The experimental method used for this purpose may briefly be described as follows: A leaf or the fruit of a plant is brought in contact on two points with two solutions of the same salt (*i. e.*, KCl) in different concentrations; the two salt solutions are connected by means of impolarizable electrodes to a measuring instrument and the e. m. f. observed. This e. m. f. depends on the ratio of the two concentrations according to Nernst's formula. *The observation that a similar e. m. f. can be produced without metals or without tissues by means of a pure organic substance (salicylic aldehyde) was the first step which led the author to a systematic study of cell combinations with immiscible substances.* Naturally not all of these combinations have a direct bearing on electrophysiological problems, but they serve to give a more complete knowledge of the fundamental phenomena upon which electrophysiology is ultimately based.

These investigations may also interest the organic chemist since it is found that the chemical constitution of the organic substances plays a most important role in their action in such cell systems. Such a combined application of organic and physical chemistry is able to solve problems which hitherto have been looked at as strictly vital.

2. Since cell combinations of the kind described have been very rarely investigated by previous authors it[1] may be well to describe first the experimental method. The apparatus used is sketched in Fig. 1. An S-shaped
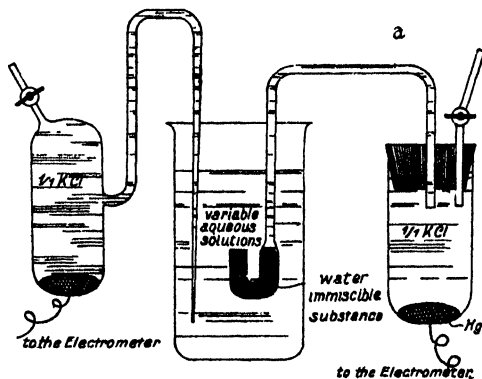
Fig. 1.

tube (*a*) is connected on one side with a calomel electrode; it is filled in the upper part with 1/1KCl solution and in the lower broader part with salicylic aldehyde which is saturated with salicylic acid. This lower part is then immersed in a series of beakers containing various solutions. Another calomel electrode is connected by means of a syphon

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[1] Among these investigations I wish to mention here those by M. Cremer, "On Nitrobenzene Diphasic Cells" [*Z. Biol.*, **47**, 1 (1906)] and those by Haber and Klemersiewig's "On Benzene (and Toluene) Cells" [*Z. physik. Chem.*, **47**, 385 (1908)]. Some hypotheses put forward by these authors will be discussed in the following papers.

with this beaker and the e. m. f. of the arrangement is observed with various solutions successively.

If we immerse the tube containing salicylic aldehyde successively in series of KCl solutions of varying concentrations, the following is observed:

Concentration of the KCl in which the tube was immersed.	E. M. F. observed in millivolt.	Time in minutes allowed for observation.
$M/10$	$+12$ to 13	$0'$ to $1'$
$M/50$	$+37$	$3'$ to $4'$
$M/250$	$+62$	$7'$ to $9'$
$M/1250$	$+96$	$11'$ to $12'$
$M/6250$	$+137$	$17'$ to $19'$
$M/1250$	$+96$ to 95	$20'$ to $23'$
$M/250$	$+61$ to 60	$26'$ to $73'$
$M/50$	$+32$ to 31	$78'$ to $81'$
$M/10$	$+7$	$84'$ to $86'$
$M/2$	-14	$88'$ to $90'$
$2.5\ M$	-32 to 33	$95'$ to $97'$
$M/2$	-15	$103'$ to $104'$
$M/10$	$+7$	$107'$ to $108'$

(The sign signifies the polarity of left side in diagram.)

These figures show to which degree such measurements are accurate and reproducible.

The change of the e. m. f. of the system can only be due to the change of a potential difference located at the junction of the salicylic aldehyde and the aqueous solution; the potential difference located at the junction of the $1/1$ KCl solution of the calomel electrode and the variable KCl solution is practically zero and constant as the velocity of migration is practically equal for $K^{\cdot}$ and Cl'.[1]

The magnitude of this change is as follows:

Between $2^1/_2\ M$ and $M/2$ 18 Millivolt
        $M/2$ and $M/10$ 21 Millivolt
        $M/10$ and $M/50$ 24 Millivolt
        $M/50$ and $M/250$ 28 Millivolt
        $M/250$ and $M/1250$ 34 Millivolt
        $M/1250$ and $M/6250$ 41 Millivolt

As the ratio of the concentrations is $1 : 5$ in all cases, the value calculated from Nernst's formula would be $58 \ln 5 = 40$ millivolt; it is seen that the values observed gradually approach this value with decreasing concentrations. It is important that this observation can be explained on the basis of theoretical considerations as shall be explained later.

These observations on cells containing salicylic aldehyde as a middle conductor also were the first instance of the artificial imitation of the

[1] A well-known theory of Nernst states that this diffusion potential equals $\dfrac{u - v}{u + v} \dfrac{RT}{F} \ln \dfrac{c_1}{c_2}$, since in our case u and v are practically equal, the diffusion potential is zero in all cases.

electrode-like potential differences between some living tissues and aqueous solutions, for the magnitude and direction of the e. m. f. is the same in both cell arrangements.

— concentrated salt solution   plant   diluted salt solution +
— concentrated salt solution   salicylic acid   diluted salt solution +

Further investigations have shown that a number of other water-immiscible liquids show a similar behavior, e. g., fatty acids mixed with substituted phenols.[1]

3. The theoretical explanation for these phenomena given in previous communications was based on a thermodynamic formula of Nernst and of Haber, stating that the potential difference at the junction of two immiscible electrolytic phases (such as an aqueous solution and salicylic aldehyde) equals RT/nF ln c_1/c_2, const. where c_1 and c_2 signify the ionic concentrations of the *same* ion in the two respective phases, *i. e.*, the K˙ concentration in water and in the salicylic aldehyde. The latter is due to a partition or slight solubility of the K˙ salt in the salicylic aldehyde. The partition of KCl between water and salicylic aldehyde is, however, not satisfactorily explained by the simple well-known law of partition, according to which the K˙ concentration in water and in salicylic aldehyde (c_1/c_2) should be constant. For if this were so, the potential difference should *not* change if the aqueous concentration is changed, according to the thermodynamic formula cited above. The fact that the potential difference does vary indicates that the partition is of a more complicated nature. The assumption was put forward in previous papers of the author that a chemical reaction between salicylic acid (in the aldehyde) and KCl was the cause of the complicated partition. This view was supported by other observations based upon measurements with various other water-immiscible electrolytic conductors.

In the following papers these theories will be also controlled by measurements of the conductivity in the non-aqueous phase, by measurements by distribution and various electromotive phenomena not described previously.

4. A brief review seems also justified concerning the thermodynamic derivation of the fundamental formula $E = RT/nF$ ln c_1/c_2 const. (cited above) at phase junctions.[1] In order to derive this formula we consider

[1] This formula was first put forward by Nernst (*Z. physik. Chem*, **9**, 385 (1892)). Haber, however, first described those experiments which showed the usefulness of this theory in a way which was not easy to predict from Nernst's theoretical explanations (*Ann. Physik.*, [4] **26**, 947 (1908)). Compare also Beutner, *Trans. Am. Electrochem. Soc.*, **21**, 2191 (1912).

a cell system of the following general type:

metal | phase I containing M˙ | phase II containing M˙ | metal (as before).

[1] J. Loeb and R. Beutner, *Biochem. Z.*, **51**, 288 (1913).

(M' denotes electrolytic ions of the metal which acts as the electrode at both ends.) *It is supposed that the two electrolytic phases are in equilibrium with each other as well as with the metal. Then the e. m. f. of the whole cell must equal zero, since it is not possible to bring about any change in this system even with a current passing through it.* This simple fact makes it possible to calculate the potential difference located at the junctions of the electrolytic phases. The potential difference between the left-hand electrode and Phase I is, according to Nernst's theory, RT/nF ln c_1 . const.' (where c_1 is the ionic concentration of M'), and the potential difference between the right-hand electrode and Phase II is RT/nF ln c_2 . const."

As the total e. m. f. of the system must be zero, the difference of these two volumes must equal the e. m. f. located at the junctions of the two phases. This difference is RT/nF ln c_1/c_2 . const.$_1$/const.' or RT/nF ln c_1/c_2 const., as stated above.

We therefore conclude that the potential difference at the junction of the two phases does not depend, in any way, on ionic mobility as does the potential difference between miscible solutions, but must have properties characteristic of potentials at metallic electrodes.

Haber[1] first devised a method for directly demonstrating this property of "phase potentials." The feature of the method is that one of the concentrations c_1 and c_2 is maintained constant, while the other is varied. This can be done, if the salt whose concentration is varied is soluble in one phase only.

To fulfil this condition he used as Phase I an aqueous solution of $HgNO_3$ and as Phase II an insoluble salt with the same ion, for instance, HgCl. The e. m. f. of the following combination is measured:

Calomel electrode | solid HgCl | $HgNO_3$ aqueous solution | Calomel electrode

If the concentration of the $HgNO_3$ solution in this cell is varied, the ionic concentration of the solid HgCl layer will not be affected. Nor will it have any considerable effect on the potential difference between the $HgNO_3$ solution and the right-hand calomel electrode, since no "phase potential" exists there. Hence the e. m. f. of the whole system must vary with the Hg· concentration according to the logarithmic law, just as in the case of a metallic electrode.

This was shown by experiment to be very exactly true. The concentration of Hg· was changed over a large range by employing NaCl solutions saturated with HgCl (instead of the $HgNO_3$) solution. As is well known the Hg· concentration of such a NaCl solution is exceedingly small and yet very accurately defined.

Experiments of the same kind were made with other insoluble salts, like AgCl and $CaSO_4$, and their ions in aqueous solution, and the same results were obtained.

[1] *Loc. cit., Ann. Physik*, **26**, 947 (1908).

Further, Haber and Klemensiewicz[1] made experiments on phase potentials of this kind varying the $H^{\cdot}$ concentration. Both phases contained water in their experiments. For instance, if Phase I is ice, and Phase II is water, then only in Phase II acids and bases are soluble, permitting a variation of the $H^{\cdot}$ concentration. For Phase I, instead of ice, such materials as glass or solutions of water in organic solvents (like benzene) were taken. Haber's hypothesis, however, that potential differences existing in living tissues are also reversible for $H^{\cdot}$ ions could not be verified.

5. It may be remarked that another interesting investigation, which illustrates the similarity between e. m. f. at phase junctions and at metallic electrodes, relates to cell systems built up from solid salts.[2] By means of such cells it is possible to measure the free energy of reactions between solid salts without the aid of metals. Recently the author has carried this idea one step further by discussing the question whether definite chemical reactions could be subjected to a measurement of their e. m. f. by means of cell systems containing phase junctions. The result of this (theoretical) investigation is that even such reactions could be measured as the formation of a salt hydrate from a solid salt and water. Such electrometric measurements have never been carried out previously, because the electric function of the phase junction has been entirely disregarded, the usual electrochemical investigation bearing only on cells with aqueous electrolytes and metals.

It seems probable that the helpless condition of the electrophysiologist, when endeavoring to utilize the results of physical investigations in his own science, is also due to the restricted applicability of the older electrochemistry. The following sentence quoted from L. Herrmann's handbook of physiology[3] expresses the realization of what has till now been lacking. He says on page 170 "The hope of gaining an understanding for the physical nature of the potential differences mentioned has not so far been fulfilled."

NEW YORK, N. Y.

STUDIES ON A NEW KIND OF E. M. F.
II. Cell Arrangements of Aqueous and Nitrobenzene Solutions Containing One Common Ion in Both Phases.

By REINHARD BEUTNER.

(1) The experiments and the theoretical considerations described above have proved the existence of interphase potential differences with properties resembling electrode potentials. The nature of (diffusion) potential differences existing in non-aqueous solutions at the contact of two different ionic concentrations will be discussed in this paper.

[1] Z. physik. Chem., 67, 385.

[2] Compare Beutner, Z. Elecktrochem., 15, 433 (1908).

[3] 14th Edition, Berlin, 1910.

The study of aqueous solutions has shown that such diffusion potentials depend on the velocity of migration of positive and negative ions; the theory of Nernst and Planck which makes their calculation possible, is well understood. At the junction of two electrolytes of different concentrations the potential difference (according to this theory) equals

$$E = \frac{u - v}{u + v} \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

An appreciable diffusion potential can therefore occur in such cases only where the velocities of the negative ion (v) and the positive ion (u) are so different that the quantity $u - v/u + v$ is of considerable magnitude; such is not the case in aqueous solutions (with the exception of acids and bases only). It will be shown in this paper that electrolytic solutions in nitrobenzene exhibit a behavior similar to aqueous solutions. The e. m. f. of systems composed of aqueous and water-immiscible electrolytes is, therefore, primarily due to the potential differences existing at the junction of the immiscible phases.

I. Objections to Ostwald's Theory of Selected Ionic Permeability and to Cremer's Experiments.

(2) This fact is contradictory to the conception of some physiologists who, recognizing the possible importance of water-immiscible layers (or membranes) for the production of electric currents by tissues, have tried to explain their action by assuming that the positive and negative ions have a very different mobility in these membranes, thus producing diffusion potentials. This view is based upon a hypothesis, put forward in a preliminary form by Ostwald,[1] according to which a selective ionic permeability of membranes is the cause of physiological currents. This hypothesis was not, however, accepted by most physical chemists and was disproved by Walden[2] working in Ostwald's own laboratory.

The observation, which Ostwald quotes in support of his hypothesis, can be easily explained in some other way, i. e., the precipitation 'of Cu metal which he describes may be a kind of stenolysis, also the polarization observed is not necessarily due to an impermeability for kations. The one-sided passage of current observed on the boundary of coagulated protein and a precipitating aqueous solution may simply be due to a high specific resistance of the layer of precipitate or membrane, which is formed or dissolved according to the direction of current.

Nevertheless, the theory was accepted by some physiologists.[3]

[1] Z. physik. Chem., 6, 71 (1890).

[2] Walden, Ibid., 10, 699 (1892). Compare also Tammann, Göttingen Nachrichten, 6, 213 (1891). Nernst objects to the theory of selective ionic permeability from a theoretical standpoint (Pflüger's Archiv., 122, 307 (1908)).

[3] Compare Höber, Physikalische Chemie der Zelle und Gewebe, Liepzig, 1911 (page 477 f.f.) (Bernstein's membrane theory).

M. Cremer[1] tried to make Ostwald's conception of a selective ionic permeability of the "membranes" clearer by means of the assumption described, according to which the mobility of the positive and negative ions in the membrane is largely different. In order to find an experimental proof for this view he experimented on solutions of picric acid in nitrobenzene and measured the e. m. f. of the following arrangement:

+ $M/8$ NaCl solution | *Nitrobenzene* $M/8$ NaCl aqueous
                saturated with   without picric   solution—
                picric acid   acid
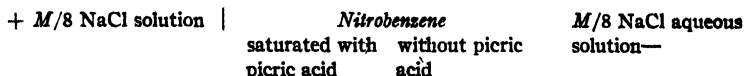
    obs.: o. 1 volt (not constant)

If really the change of the concentration of the picric acid in the nitrobenzene causes this e. m. f. (diffusion potential) the conclusion would seem necessary that the anion of the picric acid has a very much larger mobility than the H·. This result would certainly be most striking, for in aqueous solutions the velocity of the H· ion far exceeds that of all anions, as is well known. Therefore, all arrangements

      — concentrated acid   —   diluted acid +
          (aq.)   (aq.)
                           or
      — concentrated acid   —   pure water +
          (aq.)
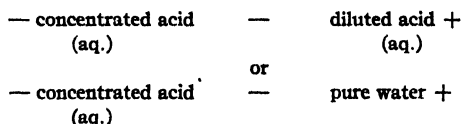
produce e. m. f. of the opposite direction.[2]

It is possible, however, to show that diffusion potentials and ionic mobilities have nothing, or very little, to do with the e. m. f. produced by Cremer's nitrobenzene cell, but that the junction of the aqueous solutions and the nitrobenzene produces nearly the total e. m. f. of the system, *for the nitrobenzene saturated with picric acid takes up sodium salts to a much larger extent than nitrobenzene containing no picric acid, and large interphase potential differences must be produced in this way, which account for the e. m. f. observed.*

To prove this, nitrobenzene with and without addition of picric acid was shaken for 15 hours with $M/8$ sodium chloride solution, resp., with water and the increase of conductivity was measured. It was found that the conductivity of pure nitrobenzene was approximately the same whether it was shaken with water or with sodium chloride solution; the conductivity observed was very small in both cases and difficult to determine accurately (about 0.015 rec. megohms). A 20% solution of picric acid in nitrobenzene however, showed a marked increase in conductivity:

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[1] *Z. Biol.*, **47**, 1 (1906).

[2] It must be said that Cremer himself seems doubtful as to whether really the ionic mobilities of positive and negative ions are reversed in nitrobenzene. He proposes his explanation as a working hypothesis only; his interesting investigation does not become less valuable therefor by the modified explanation given here.

20 cc. 20% picric acid in nitrobenzene shaken for 15 hours at room temperature with 100 cc. distilled water: 3.26 rec. megohms (at 25°).

20 cc. 20% picric acid in nitrobenzene shaken under the same conditions of temperature with 100 cc. $M/8$ NaCl solution: 4.73 rec. megohms (at 25°).

This difference of conductivity is likely to be due to formation of sodium ions in the nitrobenzene in the second experiment, or to the formation of a sodium picrate.   This is supported by the observation that pure nitrobenzene shows an increase of conductivity of the same order of magnitude after shaking with a very dilute sodium picrate solution:

20 cc. nitrobenzene shaken under the same conditions as above with 100 cc. of a $M/100$ sodium picrate solution: 3.7 rec. megohms (at 25°).

Another proof for this formation of sodium picrate is found in the fact that the solution of picric acid behaves similarly to salicylic aldehyde; in contact with aqueous sodium chloride solutions of different concentrations the potential difference changes in the same direction; the conclusions mentioned on page 2043 tend to show that this phenomenon also is due to a formation of sodium picrate, dissolved in the nitrobenzene to some extent when equilibrium at the phase junction is established.

Cremer's cell arrangement is therefore a concentration cell with respect to Na· ions: .

+ aqueous $M/8$ NaCl	*Nitrobenzene* high Na· concen- low Na· con- tration due to centration picric acid	aqueous $M/8$ NaCl —
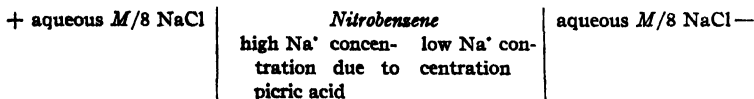
The direction of the e. m. f. of this system would be such as indicated, a quantitative calculation is scarcely possible as the system is not well defined.

Since, in this case, the junction of the aqueous and the nitrobenzene solutions produces the e. m. f., and not the·junction of the two different nitrobenzene solutions, no conclusions concerning a largely different mobility of *positive and negative ions* in nitrobenzene can be drawn.

II. Ionization in Nitrobenzene.

(3) The starting point of the experiments described in this paper are measurements which make a direct application of the fundamental formula

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

const. at phase junctions possible, and allow the deduction of clear conclusions.   Something about the ionization in the nonaqueous solvent must be known for this purpose.[1]

Although we are very well informed concerning ionic concentrations of aqueous solutions, very little is known concerning ionic concentrations in

[1] Nitrobenzene is chosen as the water-immiscible solvent in most of the experiments, as it may be secured at low cost in large quantities and produces a sufficient conductivity to make measurements of the e. m. f. possible.

all organic solvents which mix incompletely with water. The reason is that the methods and laws established for aqueous electrolytes are not always otherwise applicable, as investigations on conductivity of non-aqueous solutions have demonstrated. Some preliminary tests were, therefore, undertaken for the purpose of determining which substances would produce a particularly high electric conductivity if dissolved in a water-immiscible organic fluid. *It was found that all bases and acids, even those* which are the best conductors in aqueous solutions (like picric acid), never produce any appreciable conductivity in substances like phenol, nitrobenzene or benzaldehyde; mixtures of acids and bases, how-ever, have a conductivity which, in a $1/1$ g. molecular solution is about one hundred or one thousand times larger; this is without doubt due to the formation of a salt-like compound, just as in aqueous solutions salts may have a higher conductivity than the (weak) acids and bases from which they are formed. It seems, therefore, as if all acids and bases are "weak" electrolytes in water-immiscible solvents. The comparatively high conductivity of salts exists in both cases in a qualitatively similar fashion.

These electrical properties of nonaqueous solutions can best be demon-strated with substituted anilines as bases; a strong acid like salicylic acid or picric acid must also be employed.

The following approximate measurements may serve as an example: The nitrobenzene employed without additions had a specific conductivity of 0.01 rec. megohms at 30°; dissolving dimethyl-*o*-toluidine in a molecular concentration (135 g. in a liter) increased the conductivity up to 0.09 rec. megohms ($t = 30°$); dissolving salicylic acid (molecular concentration) alone increased up to 3.5 rec. megohms ($t = 65°$).[1] A nitrobenzene solution, however, which contained both dimethyl toluidine and salicylic acid in a molecular solution showed a conductivity of *450* reciprocal megohms. This very large increase in conductivity is certainly due to a formation of a salt-like combination (dimethyl toluidine salicylate) which dissociates into dimethyl toluidine kations and salicylic acid anions. Nothing definite concerning the degree of ionization can, however, be determined by means of measurements of conductivity.

(4) Another proof for the presence of dimethyl toluidine kations and salicylic acid anions in this mixture can be found by means of electrometric measurements. The potential difference at the junction

Nitrobenzene containing dimethyl tolui-	Sodium salicylate in water (concentration
dine and salicylic acid in a mol. con-	varied)
centration	

was measured by means of the apparatus described in Fig. 1. Instead

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[1] At 30°, salicylic acid is not sufficiently soluble for a molecular solution; it may be supposed, however, that the conductivity at 30° would be even smaller.

of salicylic aldehyde the nitrobenzene solution was filled in the U-tube. Using solutions of sodium salicylate the following e. m. f. were observed (constant, at room temperature).

	Concentration of sodium salicylate solution.		
	1/1 n.	1/2 n.	1/4 n.
E. m. f.	+0.0705 volt	+0.053 volt	+0.0355 volt

This change of the e. m. f. is exactly what would be expected according to the interphase formula if salicylic acid anions were present in the nitrobenzene:

$$E = \frac{RT}{F} \ln \frac{c_{sal.'} \text{ in nitrobenzol}}{c_{sal.'} \text{ in water}} \cdot \text{const.}$$

If the concentration in nitrobenzene is kept constant, and the aqueous concentration doubled, the potential difference should increase (the water becomes more positive). $58 \ln 2 = 17.5$ Milli-volt, which is exactly the value observed.[1]

It is seen that by changing the aqueous concentration in this system, not only the potential difference at the nitrobenzene-water interphase* might vary but also the diffusion potential between the 1/1 KCl calomel electrode and the sodium salicylate, the change of the latter, however, can be practically neglected, since K* and Cl' and also Na* and salicylic anion have very nearly the same migration velocity in aqueous solutions.

The total change of the e. m. f. observed, therefore, should be located at the nitrobenzene-water interphase and can be calculated according to the formula cited above

If, however, the concentration of the sodium salicylate solution is decreased still further the e. m. f. decreases to a smaller amount:

Change of the concentration from: Change of e. m. f.[2]

1/4 to 1/8	0.015 volt
1/8 to 1/16	0.014 volt
1/16 to 1/32	0.010 volt
1/32 to 1/64	0.006 volt
1/64 to pure water	· 0.006 volt (not constant)

This apparently is due to the fact that also pure water in contact with our nitrobenzene solution must contain salicylic acid anions owing to partition of dimethyl toluidine salicylate or salicylic acid alone between water and nitrobenzene; the concentration of the salicylic anion in water cannot be decreased below this value and therefore the potential difference does not decrease steadily but reaches a minimum value, which is determined by the distribution of the salicylic acid in the equilibrium.

In order to determine the amount of salicylic acid anions present in water in equilibrium, the nitrobenzene solution was shaken with an equal volume of distilled water, and the conductivity of the water determined ($= 2.7 \cdot 10^{-4}$) (at $t = 30°$); assuming

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[1] This calculation is only correct if the diffusion potential of the aqueous solution is zero, as the system really measured is the following:

— calomel electrode   nitrobenzene   cont.   aqueous   solution   calomel electrode +
                      dimethyl   toluidine   containing   sodium
                      and, salicylic   acid   salicylate (varying
                      ⌞ (concentration)   concentrations)
                                        2

[2] All these values are constant and reversible with the exception of the last one, which is rather difficult to determine.

that the ionic mobility of the dimethyl toluidine kation and of salicylic acid anion equals 40, the order of magnitude of the ionic concentration may be estimated from this to equal about o 03 m [1]

This value must be added, therefore, to the concentration of the anion due to dissociation of sodium salicylate, which is practically equal to the total concentration of sodium salicylate   Therefore,

A change of the concentration	Really corresponds to a change of the concentration	Calculated change of e m f
from 1/4 to 1/8	from o 28 to o 155	o 0148 volt
from 1/8 to 1/16	from o 155 to o 093	o 013 volt
from 1/16 to 1/32	from o 093 to o 061	o 010 volt
from 1/32 to 1/64	from o 061 to o 045	o 0065 volt
from 1/64 to pure water	from o 045 to o 030	o 010 volt

It is seen that these values agree with those observed

The presence of dimethyl toluidine kations in our nitrobenzene solution can be proved in an analogous way by measuring the potential difference at the junction

Nitrobenzene containing dimethyl toluiline + salicylic acid, *const*	Dimethyl toluidine hydrochloride [2] in aqueous solution

The common ion should be in this case the positive ion (dimethyl toluidine kation), therefore, by changing the aqueous concentration the change of the e. m. f. observed should be opposite to that observed with sodium salicylate in the aqueous solution, the magnitude of the change should be about the same.   The result of the measurement confirmed this as the following data show:

Molecular concentration of the dimethyl toluidine hydrochloride	E M F observed	Difference
1/1	—o 068 volt	
		>o 0155 volt
1/2	—o 0525 volt	
		>o 0145 volt
1/4	—o 038 volt	
		>o 013 volt
1/8	—o 025 volt	
		>o 009 volt
1/16	—o 016 volt	
		>o 006 volt
1/32	—o 010 volt	
		>o 002 volt
1/64	—o 008 volt	

[1] The total concentration of salicylic acid was found by means of titration with phenolphthalein to equal o 055 m   Only one-half of the total amount is, therefore, electrolytically dissociated   Since there must be, however, a slight hydrolytic splitting, producing free acid and free salt, both of which have a slow degree of ionization, the rather low degree of electrolytic dissociation *in toto* might be explained

[2] The aqueous solution of dimethyltoluidine hydrochloride was prepared by shaking the calculated quantity of the base with hydrochloric acid   Owing to hydrolytic dissociation this salt partly decomposes and a part of the base is left undissolved

The magnitude of the change of the e. m. f. observed is slightly smaller here than in each case with observations on sodium salicylate. This is difficult to account for by a quantitative theory as the equilibria in this system are also complicated through the hydrolytic splitting of dimethyl toluidine hydrochloride in aqueous solution, diffusion potentials may also be produced in the aqueous solution by this hydrolysis. In order of magnitude, the approach towards a limiting value at low concentrations and the direction of the change of the e. m. f. are a sufficient proof for the assertion.

III. Nitrobenzene Concentration Cells and the Magnitude of Diffusion Potentials in Nitrobenzene.

(5) *Summarising the results obtained so far, we have proved the existence of dimethyl toluidine kations and salicylic acid anions in a nitrobenzene solution of this base and this acid: (1) by measurements of conductivity, (2) by studying the electrode-like action of the nitrobenzene solution. Those experiments will now be described in which the ionic concentration of the nitrobenzene solution is changed while the aqueous concentration is kept constant. Nitrobenzene solutions, of the kind described, with considerable conductivity will be used for these concentration cells; it can be proved that no, or very small, diffusion potentials occur at the junction of two nitrobenzene solutions of different concentration.* The method used is as follows:

According to the theory the potential difference at the junction of the nitrobenzene solution and aqueous solution should change in opposite directions whether the ion common to both phases is an anion or a kation; the potential differences located at the phase junctions

   (1) *Nitrobenzene* containing dimethyl   Aqueous solution of sodium salicylate
         toluidine + salicylic acid,

resp.

   (2) *Nitrobenzene* containing dimethyl   Aqueous solutions of dimethyl toluidine
         toluidine + salicylic acid   hydrochloride

should therefore react in an opposite sense to a dilution of the nitrobenzene solution.

This conclusion could be easily verified by measuring the cell arrangements

$-M/5$ sodium salicylate aq solution	Nitrobenzene containing dimethyl toluidine salicylate		$M/5$ sodium salicylate + aq. solution
	$M/1$	$M/10$	

obs.: $o\ o31$ volt, (constant) at room temperature (20°)

and

$+ M/5$ dimethyl toluidine hydrochloride aq. sol.	Nitrobenzene containing dimethyl toluidine salicylate		$M/5$ dimethyl toluidine hydrochloride aq. sol.
	$M/1$	$M/10$	

obs.: $o.035$ volt (constant), at room temperature (20°).

The apparatus used for these measurements is described in Fig. 2, which requires no further explanation. (The connection from both aqueous solutions to the measuring instrument electrometer was made by means of calomel electrodes which did not produce any new e. m. f., since diffusion potentials existing in the aqueous solutions must be equal and opposite.)

In the first cell the more concentrated nitrobenzene solution is on the negative pole (reversibility for anions), in the second on the positive (reversibility for kations).

Comparing these concentration cells with those known in earlier electro-chemistry we may say that the metallic electrodes are replaced here by the aqueous solutions while the two nitrobenzene solutions replace the two aqueous solutions usually employed. *These observations furnish a striking contradiction to the theory that diffusion potentials of considerable magnitude exist at the junction of two different nitrobenzene solutions. If this were so, and if the interphase potential differences played no role, the direction of the e m f. would be the same in the two cell arrangements de-*

$M/5$ aqueous solution of sodium salicylate (or of dimethyl toluidine hydrochloride)

$M/5$ aqueous solution of sodium salicylate (or of dimethyl toluidine hydrochloride)

$M/10$ nitrobenzene solution of dimethyl toluidine + salicylic acid

$M/1$ nitrobenzene solution of the same
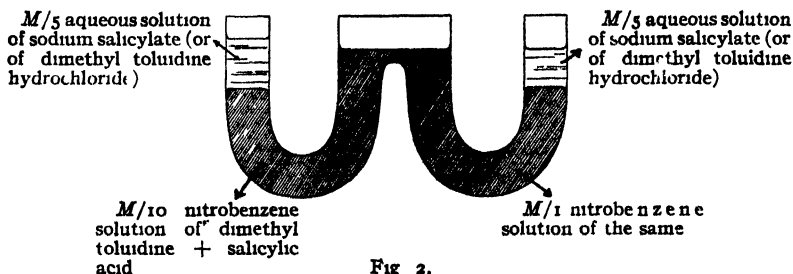
Fig 2.

scribed, i. e., it would not be possible to reverse the direction of the e. m. f. by changing the aqueous solutions (replacing sodium salicylate by dimethyl toluidine hydrochloride), *as is actually the case.*

The question, however, presents itself whether the total e. m f. observed is located at the nitrobenzene-water interphases a, b, a' and b' exclusively or whether a small additional diffusion potential is also produced at the junction of the two nitrobenzene solutions of different concentration (x). This problem can be solved approximately in the following way·

The e. m. f of the first cell (concentration cell with respect to salicylic acid anions) equals $(0.058 \lg c_1/c_2) + x$ volts at room temperature, if c_1 and c_2 are the concentrations of the anions of salicylic acid in the two nitrobenzene solutions the e. m. f. of the second cell (concentration cell with respect to dimethyl toluidine kations) equals $0.058 \lg c_1'/c_2' - x$ volts if c_1' and c_2' are the concentrations of the kations in the two nitro-benzene solutions.

Now if $c_1 = c_1'$, resp., $c_2 = c_2'$, i. e., if the concentration of the dimethyl toluidine kations equals the concentration of the salicylic acid anions in both nitrobenzene solutions at the junction of the aqueous solutions, we can calculate the magnitude of the diffusion potentials from the difference of the e. m. f. observed; the difference of the e. m. f. of the two cells (0.035–0.031 volts) would then equal $0.058 \lg c_1/c_2 - 0.058 \lg c_1'/c_2' + 2x$ or $x = 0.002$ volts.

Apparently the assumption of the equality of c_1 and c_1', resp., c_2 and c_2' is justified if the nitrobenzene contains no other electrolyte than dimethyl toluidine salicylate (no sodium salicylate, resp., no dimethyl toluidine HCl). A certain quantity of the electrolyte present in the *aqueous* solution will, however, penetrate into the nitrobenzene at the phase junction until equilibrium of distribution is established, but this amount must be so small that the ionic concentration in the nitrobenzene is not considerably changed. In the experiments described, all the concentrations were selected in such a way that this is actually the case. This can be proved by means of measurements of conductivity, the conductivity imparted to pure nitrobenzene after shaking with the aqueous solutions is so small that it can be neglected as compared with the own conductivity of the nitrobenzene solutions used (as the following figures show)

Conductivity of the mol solution in nitrobenzene	450	rec Megohms
Conductivity of the $M/10$ solution in nitrobenzene	84	rec Megohms
Conductivity of nitrobenzene after shaking with a double volume of $M/5$ sodium salicylate (for six hours)	0 6	rec Megohms
The same after shaking with $M/5$ dimethyl toluidine HCl	1 5	rec Megohms

The highly conducting nitrobenzene solutions were also shaken with the two aqueous solutions A slight decrease in conductivity was observed in this case [from 450 to 430 rec megohms (sod salic), resp, 420 (dimethyl tol HCl), and from 83 7 to 83 (sod salic), resp, 83 (dimethyl tol HCl)] The cause of this decrease is hard to define We are certainly justified, however, to conclude from these measurements that the ionic concentrations in nitrobenzene are not changed considerably by distribution equilibrium at the phase junction in question, and that therefore *the calculation of the diffusion potential is correct $x = 0 002$ volts* or only a small fraction of the total e m f observed [1]

Conductivity of $M/5$ dimethyl toluidine HCl	0 017 rec ohms
Conductivity of $M/5$ sodium salicylate	0 012 rec ohms
Conductivity of water after shaking with the mol nitrobenzene sol	0 0023 rec ohms
The same after shaking with the $M/10$ nitrobenzene solution	0 0006 rec ohms

This is of importance for quantitative calculation of the e m f described below

(6) Similar experiments were performed with other substances; for instance, the following arrangement was measured:

[1] The ionic concentration of the two aqueous solutions in our experiments is not changed either by the electrolytes diffusing *from* the nitrobenzene solution *into* the aqueous phase at the phase junctions, as the following data show

— $M/5$ sodium nitroben- zoate aq sol	Nitrobenzene containing di methyl aniline and m nitro- benzoic acid	$M/5$ sodium nitroben- zoate + aq sol
	$M/1$ $M/10$	

obs o 037 volt (constant)

+ $M/5$ dimethyl aniline hydrochloride aq sol	Nitrobenzene containing di methyl aniline and m nitro- benzoic acid	$M/5$ dimethyl toluidine hydrochloride
	$M/1$ $M/10$	

obs o 03 volt (constant)

The diffusion potential between the two nitrobenzene solutions would equal zero in this case, as the e. m. f. of the two systems is equal and op- posite.

(7) We may conclude from these experiments that ionic mobilities and diffusion potentials exhibit similar properties in aqueous and nitrobenzene solutions and that there is no reason to suppose that a relatively excessive

Nitrobenzene solu- tion of varying con- centration
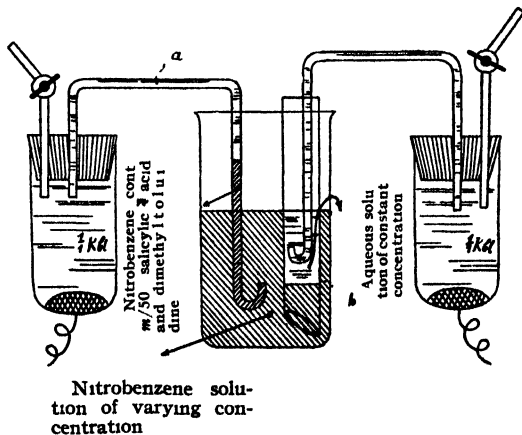
Fig 3

velocity of certain ions produces particular effects in systems of immiscible electrolytic conductors. Interphase potential differences determine the magnitude and the direction of the e. m f. in all such systems.

Concerning electrophysiological theories it can be said, that the results obtained are in direct contradiction to the theory of selective ionic perme- ability. This theory is applied by some physiological authors in rather vague theoretical considerations, explaining various visible changes in living cells through an invasion of positive and negative ions due to an alleged mobility or permeability of the ion in or through the cell mem- brane. The experiments described furnish proof against such theories by means of the evidence that no essential difference exists between + and — ions in water-immiscible solvents so far as the mobility is concerned.

(8) *A quantitative calculation of the e. m. f. of our concentration cells from the ratio of the ionic concentrations* should be possible in the same way as with the ordinary concentration cell. If we 'assume that the ionic concentration in the nitrobenzene is proportional to conductivity, the e. m. f. calculated would be 0.058 lg c_1/c_2 volts, where c_1 and c_2 are the conductivities of the two nitrobenzene solutions: c_1 = 450 rec. megohms, c_2 = 83 rec. megohms; e. m. f. therefore should be 0.042 volt; this value is not identical, however, with the one observed (0.033 volt). Owing to our incomplete knowledge concerning ionization in nitrobenzene solutions, it is difficult to account, with certainty, for this deviation; the following observations, however, may ·have some bearing on the problem: The conductivity of the grammolecular nitrobenzene solution (of dimethyl toluidine + salicylic acid) equals 430 rec. megohms only if saturated with water; the same solution in dry nitrobenzene had only 340 rec. megohms; the conductivity of the $M/10$ nitrobenzene solution, however, did not change by saturating with water. If we assume that the conductivity of the dry nitrobenzene solutions is proportional to the concentrations of those ions which act in the concentration cells (dimethyl toluidine$^\oplus$ salic.$^\ominus$) we get, in fact, a much closer agreement: 0.058 lg 340/83 = 0.035 volt, which is identical within the experimental errors with the value observed. We may assume that the increase in conductivity observed, if the molecular nitrobenzene solution is saturated on water, is due to a chemical reaction of hydrolysis resulting in the formation of H˙ ions or other ions.[1]

(9) Experiments of the same kind may be described at last with a somewhat modified experimental arrangement (see Fig. 4). By means of this arrangement the nitrobenzene-water interphase could be kept constant on one side (in the narrow tube *a*) while the other interphase (in broader tube *b*) could be changed; the change of the e. m. f. with the change of the solution then is the effect observed. This method is therefore quite analogous to the one described above (compare Fig. 1), with the difference that in this case the concentration of the nitrobenzene varied while the aqueous concentration is kept constant.

The narrow tube (*a*), connected with one electrode, is filled with 1/1 KCl (aq. sol.) in upper part and with a 0.02 M nitrobenzene solution of dimethyl toluidine and salicylic acid in the lower hook-shaped part; this is immersed into a beaker containing the same nitrobenzene solution in varying concentrations; an aqueous 0.5 M solution of sodium salicylate (or toluidine hydrochloride) supernates on the nitrobenzene in the beaker, in a broader tube (*b*), this is connected with the other calomel electrode by means of a hook-shaped tube.

With sodium salicylate as constant aqueous solution, the system really measured is:

[1] In the experiments with nitrobenzene solutions of dimethyl aniline and *m*-nitrobenzoic acid the value calculated from the ratio of the conductivities of the dry solutions is 0.054 volt (obs. ·0.037 volt). This deviation is due to a very complicated state of this nitrobenzene solution which we cannot fully account for so far; the molecular conductivity of this solution increases with increasing concentration.

| – calomel electrode (1/1 KCl) | Nitrobenzene solution of salicylic acid and dimethyl toluidine 0.02 M (constant) variable concentration | 0.5 M sodium salicylate in water | calomel electrode + |

The following e. m. f. were observed:

Concentration of the variable solution.	E. M. F.	Change c E. M. F.
M/2	0.060 volt	
		>0.028 volt
M/10	0.088 volt	
		>0.021 volt
M/50	0.109 volt	
		>0.024 volt
M/250	0.133 volt	
		>0.000 volt
M/1250	0.133 volt	

With dimethyl toluidine hydrochloride the system measured is:

| + calomel electrode | Nitrobenzene solution of salicylic acid and dimethyl toluidine 0.02 M (constant) variable concentration | 0.5 M dimethyl toluidine in water | calomel electrode – |

E. M. F. observed:

Concentration of the variable solution.	E. M. F.	Change of the E. M. F.
M/12	0 048 volt	
		>0.029 volt
M/10	0.077 volt	
		>0.029 volt
M/50	0.106 volt	
		>0.000 volt
M/250	0.135 volt	
		>0.000 volt
M/1250	0.135 volt	

It is seen that the direction of the change is opposite in both cases as the e. m. f. of the two systems are in opposite directions.

The conductivities of the dry nitrobenzene solutions were observed as follows ($t = 30°$):

M/2................................ ... 243 rec. megohms
M/10............................. ...... 80.5 rec. megohms
M/50............................. .... 15.3 rec. megohms
M/250.................................. 2.7 rec. megohms
M/1250................................ 0.4 rec. megohms

In order to calculate the change of the e. m. f. from the ratio of conductivity, it must be considered that some sodium salicylate or dimethyl toluidine passes from the aqueous solution into the nitrobenzene; it was found that the pure nitrobenzene with a conductivity of 0.006 rec. megohm had 2.4 rec. megohms after shaking with 0.5 M sodium salicylate (aq. sol.); 2.3 rec. megohms after shaking dimethyl toluidine hydrochloride. The ionic concentration in the nitrobenzene can therefore not be lowered below a value corresponding to this conductivity, which is about M/250. A dilution of

the nitrobenzene from $M/250$ to $M/1250$ can, therefore, produce no change of the e. m f as was really observed With relatively concentrated nitrobenzene solutions the salts invading from the aqueous solution can be neglected, the change of the e m f equals the one calculated from the ratio of conductivities o 5 M to o 1 M o 058 lg 80 5 = o 028 volt, (obs o 029) For the intermediate concentrations the value observed is in each case smaller than the one calculated owing to the electrolytes penetrating into the nitrobenzene from the aqueous solution,

$M/10$ to $M/50$ o 058 lg 80 5/15 3 = o 042 volt (obs o 021, o 029 volt)

$M/50$ to $M/250$ o 058 lg 15 3/2 7 = o 044 volt (obs o 029 volt)

A quantitative calculation similar to that described above for aqueous solutions does not seem possible, however, owing to our incomplete knowledge concerning distribution and ionization in nonaqueous solutions

IV. Concentration Double Cell of a New Type.

(9) Observations concerning the e. m. f. of the following concentration cell may finally be mentioned ·

— o 2 M sod salic (aq sol)	M dimethyl tol + salic acid *nitrobenzene*	o 2 M dimethyl tol
HCl (aq sol)	o 1 M dimethyl tol + salic acid *nitrobenzene*	o 2 M sod salic aq sol +
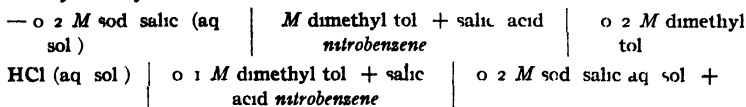
e m f observed at room temperature o 066 volt (constant)

(Concerning the experimental arrangement compare Fig. 4.)

This cell cannot contain any diffusion potentials at all according to the

$M/5$ aqueous solution of dimethyl toluidine hydrochloride

$M/5$ aqueous solution of sodium salicylate

$M/5$ aqueous solution of sodium salicylate

$M/1$ nitroben z e n e solution of dimethyl toluidine + salicylic acid

$M/10$ nitrobenzene solution of dimethyl toluidine + salicylic acid
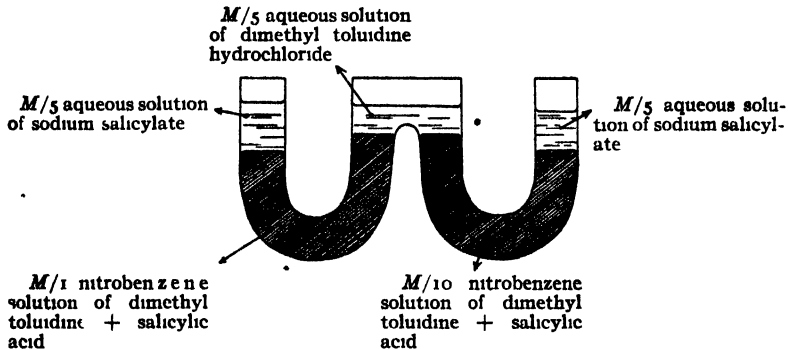
Fig 4

measurements of distribution and conductivity described above, the total e. m f. observed must be located at the four-phase junctions.

Comparing this cell with those described on page 2053, it is easily understood that the e. m. f. observed here must equal the sum of those previously described, which is actually the case· 0.031 + 0.035 volt = 0.066 volt.

A concentration double cell of this type is especially fit for arranging a *large number* of alternating nitrobenzene and aqueous layers in such a way as to produce a considerable e. m. f. because the same aqueous solution is at both ends of the cell, and also because it contains no diffusion poten-

tials at all. Experiments concerning such cell arrangements will be communicated later.

Summary.

(1) The e. m. f. of cell arrangements consisting of aqueous and nitrobenzene solutions is measured; the solutions which are in contact with each other always contain one common ion. This makes it most easily possible to calculate from the thermodynamic formula those potential differences which exist at the nitrobenzene-water interphase.

(2) Preliminary experiments are described, in order to test the nature of ionic conduction in nitrobenzene and in order to prove the applicability of the thermodynamic formula at the phase junctions in question.

(3) The e. m. f. of cells which consist of two nitrobenzene solutions of different concentrations in contact with each other between two identical aqueous solutions is then measured. It can be proved that the total e. m. f. of these systems is practically entirely located at the phase junctions and not at the junctions of the two nitrobenzene solutions. *This result can be understood without an elaborate theoretical explanation by contemplating the diagrams of the cells. If the e. m. f. observed was located at the junction of the two nitrobenzene solutions it would certainly not be possible to reverse the direction of the e. m. f. by changing the aqueous solutions such as is actually the case.*

(4) Ostwald had assumed that membranes or layers of water-immiscible electrolytes between two aqueous solutions produce e. m. f. owing to a selective ionic permeability; this would mean that in the membrane the mobility of the anion, *i. e.*, far exceeds that of the kation, thus producing a diffusion potential. According to this hypothesis then, the e. m. f. produced by a water-immiscible layer is not located at the phase junction but inside the layer or membrane. This theory does not agree, therefore, with the experimental results obtained here.

(5) Cremer's experiments on biphasic water-nitrobenzene cell arrangements do not support the theory of different mobilities of anions and kations, because the e. m. f. observed by him is also located at nitrobenzene-water interphases. This is due to the fact that the distribution of electrolytes between water and nitrobenzene is much more complicated than was assumed by Cremer; the salt contained in the aqueous solution invades the nitrobenzene on one side to a much larger extent than on the other side, as can be shown by means of conductivity measurements. In the experiments described here the aqueous and nitrobenzene solutions are selected in such a way that their ionic concentration is not changed appreciably by electrolytes passing from either phase into the other, if the equilibrium of distribution is established. For this reason it can be claimed that these experiments furnish a better argument for the problem in question.

DEPARTMENT OF EXPERIMENTAL BIOLOGY,
THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH,
NEW YORK.

TERBIUM.

BY C. JAMES AND D. W. BISSELL.
Received June 4, 1914.

This element was first described by Mosander during his researches upon yttria, just previous to 1843, under the name of erbium. He stated that the oxide was orange-yellow and the salts colorless.

Later, several chemists, employing the fusion of the nitrate method, failed to obtain the original erbium of Mosander, so the name erbium was given to terbium, which gave a rose colored oxide.

Delafontain maintained the existence of old erbium, or terbium as it was now called. He recommended samarskite[1] as a source of terbium, and described the preparation of a terbia of a dark orange-yellow color. The salts prepared from it were said to be colorless and to show only a trace of the absorption of didymium.

Marignac[2] fractionated 300 g. of gadolinite earths and obtained three sets of oxides: white yttria, rose erbia, and intermediate oxides of a more or less deep yellow color. He separated the didymium from these and showed that the color must be due to a third gadolinite oxide originally mentioned by Mosander and later denied by Bunsen and Bahr, and Cleve and Hoglund. Marignac's terbia, purified by the potassium sulfate method and the oxalic acid method, consisted of a dark orange-yellow powder.

Cleve[3] confirms Marignac's conclusions with regard to the existence of terbia.

Lecoq de Boisbaudron[4] pointed out the complicated nature of terbium oxide. He said that it contained variable proportions of yttria, holmia, ytterbia, samaria, erbia and the yellow earth. Such material was submitted to many fractionations. The resulting products when tested by the spectroscope showed the possibility of the existence of three terbiums, which he designated by $Z\alpha$, $Z\beta$, and $Z\gamma$. $Z\beta$ gave a very deep reddish brown terbia. The solution of the chloride gave only a weak absorption spectrum composed of the bands of dysprosium and of a band which appeared to belong to a new element. The same band ($\lambda 487.7$) appeared as strongly in the paler colored terbias, and he, therefore, concluded that it was due to another terbia which he provisionally named $Z\delta$. He was unable to fractionate further, since all the material was used up.

Boisbaudron[5] examined a sample of impure mosandria, and found that it consisted of yttrium α and terbia as Marignac had supposed.

[1] *Ann. chim. phys.*, 14, 238 (1887).

[2] *Ibid.*, 247.

[3] *Bull. soc. chim.*, 31, 195 (1879).

[4] *Compt. rend.*, 102, 153 (1886).

[5] *Ibid.*, 647.

Hoffmann and Kruss[1] showed that terbia (of this date, 1893), which cannot be split up further by means of the double sulfate or formate methods, may be fractionated by solution in aniline chloride.

Marc[2] worked upon terbium material, obtained by Weiss during the preparation of didymium from monazite by the chromic acid method of Muthmann and Bohm, and came to the conclusion that, although his terbia was colored deep brown, only a few per cent. of the element causing this was present. He also said that the solution of the oxide gave an absorption band $\lambda464$-461.

Emma Portratz,[3] in a paper on terbium and some of its compounds, describes the oxide as being of a brownish orange color like some varieties of ocher.

Feit[4] worked on the yttrium earths from monazite and obtained a crude oxide, which he supposed contained about 12% of terbia.

Urbain,[5] by three different methods of fractionation, obtained a dark colored earth between gadolinium and dysprosium, whose solutions showed the absorption band $\lambda488$. He kept, provisionally, the name $Z\delta$, given by Boisbaudron to the element possessing this property. The results of Marc were not duplicated. The latter stated that the salt~ of terbium possessed a pink color, while Urbain showed that a common colored impurity of terbium was dysprosium. The compounds of this latter element communicate a green tint to those of terbium. Urbain obtained about 100 g. of the crude dark oxides. This material was submitted to a further long and careful fractionation,[6] which gave 7 g. of an oxide, that could not be divided by continued fractionation. It gave a dark brown oxide by ignition of the oxalate, and a black oxide when the sulfate was calcined at $.1600°$. The oxide corresponded to the formula Tb_4O_7. The solution of this oxide showed the absorption spectrum of $Z\delta$, the inverse spectrum of $Z\beta$, the spark spectrum of Demarcay's Γ, and the phosphorescent spectrum of a meta element of yttrium and to $G\beta$ (Crookes). The atomic weight was found to be 159.22.

Urbain[7] states that Boisbaudron's $Z\alpha$ is identical with dysprosium. ·

Urbain and Jantsch,[8] in describing some new compounds of terbium and dysprosium, state that terbium can be weighed as the oxide Tb_4O_7 if it has not been heated to too high a temperature.

[1] Z. anorg. Chem., 4, 27 (1893).

[2] Ber., 35, 389 (1902).

[3] Chem. News, 92, 3 (1905).

[4] Z. anorg. Chem., 43, 267 (1905).

[5] Compt. rend., 139, No. 19 (1904).

[6] Ibid., 141, No. 12 (1905).

[7] Compt. rend., 143, 229 (1906).

[8] Ibid., 146, 127 (1908).

Urbain[1] concludes among other things that the elements Γ of Demarçay, Zβ and Zδ of Lecoq de Boisbaudron, Gβ, ionium, and incognitum of Sir William Crookes are identical with terbium.

Welsbach[2] fractionating the yttrium earths by means of the double oxalates with ammonium oxalate, observed that terbium was distributed between the gadolinium and dysprosium fractions. He said that the separation was tedious, but might be carried out satisfactorily. On each side of the terbium the fractions were colored deep ocher; also they gave no optical test for terbium. From this he concluded that old terbia consisted of three elements, which he provisionally named TbI, TbII and TbIII. TbI was closely related to gadolinium, and TbIII to dysprosium.

Separation.—The methods used originally gave an oxide containing only a few per cent. of terbium oxide. These processes include: fusion of the nitrates; precipitation by potassium sulfate; precipitation of oxalates from a strongly nitric acid solution; the formic acid method.

When the nitrates are partially decomposed by heat, poured into water, boiled until clear and allowed to cool and crystallize, the least basic element separates first in the form of a crystalline basic nitrate. This method is not to be recommended for the extraction of terbium.

Terbium potassium sulfate and terbium sodium sulfate are very much less soluble than the corresponding double sulfates of yttrium and erbium, etc. They are more soluble than those of the cerium metals. Owing to the similar solubilities of the double sulfates of gadolinium and dysprosium, and also to the fractional precipitation nature of the method, it is very tedious.

The fractional precipitation of the oxalate from a highly acid solution of the nitrate is practically useless.

Terbium formate is very much less soluble than yttrium formate, and the formates might be used for the separation of yttrium and terbium, if it were not for the fact that they form a double compound. Philippium formate was found to be yttrium terbium formate.

Later, Boisbaudron recommended the use of very dilute ammonium hydroxide. Urbain says this method is very tedious. He advises the following: fractional crystallization of the double nitrates with nickel; fractional crystallization of the simple nitrates in the presence of bismuth nitrate; fractional crystallization of the ethylsulfates.

The double nickel nitrate method[3] gave gadolinium nickel nitrate, in a very pure state, as the least soluble portion. The most soluble fractions gave very dark colored oxides, whose solutions showed a strong spectrum of dysprosium, a feeble spectrum of holmium, and an almost

[1] *Chem. News*, **100**, 73 (1909).
[2] *Chem. Ztg.*, **35**, 658.
[3] Urbain, *Compt. rend.*, **139**, No. 19 (1904).

imperceptible band of $Z\delta$ These solutions possessed an olive color. The middle fractions gave oxides, paler in color, and the solutions when examined by the spectroscope revealed only the band belonging to $Z\delta$.

The Fractionation of the Simple Nitrates in the Presence of Bismuth Nitrate —Urbain found that the solubility of bismuth nitrate in nitric acid to be greater than the solubility of gadolinium nitrate, but less than that of dysprosium Since bismuth nitrate is isomorphous with the nitrates of the rare earths, it would accumulate with the terbium and enlarge the amount of material, thus making it easier to carry on the fractionation The above chemist found, after a careful study, that bismuth nitrate is less soluble than the nitrate of terbium However, he was unable to separate quantitatively terbium from gadolinium, as he had done with europium and samarium by the addition of bismuth magnesium nitrate Bismuth was separated from the terbium fractions by means of hydrogen sulfide The terbium was then precipitated by the addition of a solution of oxalic acid

Fractionation of the ethylsulfates rapidly separates terbium from most of the yttrium earths This method has been extensively used by Urbain and Lacombe

The authors, after due consideration, came to the conclusion that the only methods worth trying were the last three The double nickel nitrate method must be a very good one, since, by it, Urbain obtained a pure white gadolinia This process was tried, and some difficulty was encountered in the crystallizations It requires considerable experience in order to get good crystals It is also unfortunate that the liquid is so highly colored, for it prevents observations being made with regard to changes in color of the earth solutions themselves In addition the absorption spectra cannot be studied

The crystallization of the simple nitrates was not tried, since it does not work anything like as rapidly as the bromate method The ethyl sulfates are useful It is a very great pity that they are so readily hydrolyzed

The material, for the extraction of terbium oxide, consisted of gadolinium oxide containing terbium oxide There were also present certain amounts of dysprosium and holmium oxides and traces of those of yttrium and erbium The whole was converted into bromates by warming with bromic acid The bromates so obtained were submitted to a long and careful fractionation

After a few series of operations, the whole of the terbium and most of the holmium and dysprosium were found to be in the most soluble portion As the work proceeded, a faint absorption band appeared in the blue, when the least soluble fraction was examined by means of the spec-

troscope. This was due to small amounts of europium, which showed that europium bromate was less soluble than gadolinium bromate.

Europium bromate would, therefore, appear to possess the lowest solubility of all the rare earth bromates. The solubility first of all decreases as we go up the series in the following order: lanthanum, cerium, praseodymium, neodymium, samarium, europium. After europium has been reached, the solubility commences to increase again in this manner: europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, lutecium, celtium, and scandium.

By the time a considerable number of series of operations had been carried out, the colors of the oxides of the fractions were observed to show very much light upon the rapidity of fractionation. The least soluble—gadolinium bromate—gave a nearly white oxide. All gadolinium was removed from the series, as soon as it gave an almost white oxide. With increase of solubility the color of the oxides rapidly changes. They became darker and darker until a maximum was reached, after which the colors became paler. The most soluble fractions gave a buff colored oxide. These portions were removed when this condition had been attained. From these results it can be seen that terbium is rapidly separated from gadolinium by means of the bromate method. The separation of terbium from dysprosium is not as simple as in the case of the previous element. Perhaps the ethylsulfates would be the best salts to use for this portion of the work. The results of the application of this method will be described later on.

The fractions that gave the darkest colored oxides showed only one absorption band—that of $Z\delta$ or terbium. The more soluble portions of the terbium showed the absorption bands of dysprosium in addition, while the less soluble portions gave very faint neodymium bands, the latter indicating the fact that neodymium bromate comes between the bromates of terbium and gadolinium. It would, therefore, be reasonable to conclude that by the careful use of neodymium the separation of terbium and gadolinium could be carried out quantitatively. Neodymium can, of course, be readily separated from terbium by many well known methods, such as by crystallizing the double magnesium nitrates with bismuth magnesium nitrate. Only three or four operations are necessary. Neodymium magnesium nitrate passes into the least soluble fractions, since it is practically insoluble in bismuth magnesium nitrate. The bismuth magnesium compound comes next, while the terbium magnesium nitrate collects in the mother liquor.

A statement, made somewhat recently, by another worker with regard to the bromate method, led one to understand that there was considerable difficulty in separating yttrium from gadolinium. Yttrium bromate comes between the bromates of erbium and holmium with regard

to their solubilities. It will, therefore, naturally tend to divide itself into two portions, one accompanying the erbium and the other the holmium and dysprosium. Therefore as soon as a fraction, less soluble than dysprosium, no longer gives the dysprosium absorption spectrum, it is free from yttrium. Since, in addition, terbium and neodymium come between dysprosium and gadolinium, the separation of yttrium and gadolinium must be extremely good. When we have a fraction containing yttrium more soluble than holmium and free from the absorption bands of this element, it is free from gadolinium.

The original bromates used in this work comprised many kilograms. As large amounts of gadolinium bromate were, however, rapidly removed from one end, and fair quantities of the bromates of erbium, yttrium, holmium, and dysprosium from the other, the bulk of material undergoing fractionation quickly decreased. The whole of the erbium was removed in the most soluble portion after a few crystallizations. This was followed by yttrium and holmium with some dysprosium. Finally the holmium bands became very faint, and later dysprosium, with a little terbium, formed the most soluble fractions of the series.

By this time the fractions had become reduced to about 10 g. in each. About 30 g. of very pure terbium oxalate, giving a black oxide, were ob-

Wave lengths in A.U.

Visible absorption spectrum of terbium.

Concentrated solution of Tb(NO₃)₃

tained. Thirty grams of an oxalate not quite so pure were also separated.

The crystallization of the chlorides from hydrochloric acid was used in the endeavor to separate small amounts of terbium from dysprosium. The chlorides formed very nice crystals, and the mother liquor could easily be drained off. The rate of fractionation seemed to be about the same as in the case of the nitrates. The oxide from the least soluble was darker than that from the most soluble portion. This showed that terbium chloride like terbium nitrate passed into the least soluble fractions.

When a mixture of gas and air was directed upon terbium peroxide, or upon gadolinium oxide containing terbium peroxide, heated almost to redness, the mass immediately became incandescent, and the gas usually took fire.

A strong solution of terbium nitrate gave an absorption spectrum consisting of one band in the blue as shown in the figure on preceding page.

The authors conclude from their results that there is only one terbium. By means of the bromate process, terbium is comparatively rapidly separated from gadolinium; and neodymium, if present, comes between the two. This work agrees with that of Urbain and not with that of von Welsbach.

DURHAM, N H.

THE RADIUM : URANIUM RATIO IN CARNOTITES.[1]

By S C LIND AND C F. WHITTEMORE.

I. Introduction.

The constancy of the ratio of radium to uranium in the uranium minerals, and its significance in the theory of the origin of radium have been recognized for some time. For its experimental demonstration we are indebted to the early work of Boltwood,[2] Rutherford,[3] Strutt,[4] McCoy,[5] and Eve.[6]

At a somewhat later period it began to be recognized that certain uranium minerals of secondary origin, of which autunite $(Ca(UO_2)_2(PO_4)_2.-8H_2O)$ is one of the chief representatives, show a ratio below that of pitchblende. In 1909, Mlle. Gleditsch[7] announced that she had found a sample of French autunite showing only about 80% of the normal ratio. A low ratio was confirmed in 1910 by A. S. Russell,[8] who, also in a sample of French autunite, found only 27% of the normal ratio, while Soddy and Pirret,[9] about the same time, found a sample of Spanish autunite with 44.5% of the pitchblende ratio.

To account for these low ratios in a sense consistent with the Rutherford and Soddy theory of radioactivity, two different explanations have been proposed. The first supposes that the secondary minerals are too young for the quantity of radium to have accumulated to the maximum equilibrium value shown in the older minerals such as pitchblende. The second mode of explanation assumes that the secondary minerals, owing to a looser mechanical structure, are more subject to a *leaching process* by water and that radium is more readily removed than uranium, which results in a low ratio of the former to the latter.

[1] Published by permission of the Director of the Bureau of Mines

[2] Boltwood, *Phil Mag*, 9, 599 (1905), *Am J Sci*, 18, 97 (1904), 25, 269 (1908)

[3] Rutherford and Boltwood, *Am J Sci*, 20, 55 (1905), 22, 1 (1906)

[4] Strutt, *Proc Roy Soc Lond*, (A) 76, 88 and 312 (1905)

[5] McCoy, *Ber*, 37, 2641 (1904), THIS JOURNAL, 27, 391 (1905)

[6] Eve, *Am J Sci*, 22, 4 (1906)

[7] Mlle Gleditsch, *Compt rend*, 148, 1451, 149, 267 (1909)

[8] A S Russell, *Nature*, 84, 238 (1910)

[9] Soddy and Pirret, *Phil Mag*, 20, 345 (1910), 21, 652 (1911)

Additional evidence, adduced principally by Marckwald and Russell,[1] appears to support the "leaching" theory, since the ionium uranium ratio was found much more nearly to approach theory in autunite than does the radium uranium ratio, thus indicating a removal of radium, while lead, one of the end products of the uranium family, was found to be almost entirely lacking .

At the same time that Mlle Gleditsch[2] announced the existence of a low radium uranium ratio in autunite, she reported a high ratio (about 16% high) in thorianite of Ceylon The explanation of a high ratio appeared to present much more formidable difficulties than the low ones Mlle Gleditsch favored the view that either ionium, or some other unknown member between 'uranium and radium, had a much longer period than previously supposed, necessitating a greater lapse of time for equilibrium to be attained Consequently all the uranium minerals according to this view would be slowly advancing to an equilibrium quantity of radium higher than that in most pitchblendes

This view of Mlle Gleditsch's did not find general acceptance Soddy and Pirret[2] had also examined autunite, pitchblende and thorianite, and while confirming a low ratio for autunite, as already stated, they failed to find a difference between the latter two exceeding 3%, which they regarded as within their limits of experimental error

In a later investigation extended to a much larger number of uranium minerals Mlle Gleditsch[3] confirmed her earlier results, finding ratios of radium uranium varying from $1\ 82 \times 10^{-7}$ for chalcolite of Saxony, to $3\ 74 \times 10^{-7}$ for pitchblende of Cornwall, while from two pitchblendes from Norway she reported $3\ 48 \times 10^{-7}$ and $3\ 64 \times 10^{-7}$, respectively

The most recent experimental contribution to this subject is the searching examination by Heimann and Marckwald[4] of the radium uranium ratio in eight samples from all the principal pitchblende localities of the world, including Joachimsthal, Saxony, German East Africa, Norway, Bohemia, Colorado, and Cornwall Determinations were made by two entirely different methods, the emanation method and the gamma-ray method In all eight samples constancy of the radium uranium ratio was found within $0\ 4\%$ The absolute value of the ratio was determined by comparison with a radium solution having its origin in the Hoenigschmid[5] atomic weight radium of the Institute for Radium Research in Vienna and was found to be $3\ 328 \times 10^{-7}$. The satisfactory agreement of this

[1] Marckwald and Russell, *Ber*, **44**, 771–5 (1911), *Jahrb d Radioakt u Electronik* **8**, 457 (1911)

[2] *Loc cit*

[3] Mlle Gleditsch, *Le Radium*, **8**, 256 (1911)

[4] Heimann and Marckwald, *Jahrb d Radioakt u Elektronik*, **10**, 299 (1913), *Physik Z*, **14**, 303 (1913)

[5] Hoenigschmid, *Sitzb Vienna Acad*, *Abt IIa*, **120** (Nov, 1911)

number with the theoretical value of the ratio as calculated from radiation data (see calculation by Stefan Meyer[1]) lends it a great degree of reliability.

Carnotites have been included among the specimens of uranium minerals examined by a few authors. From the results of Boltwood[2] and of McCoy,[2] no abnormally low ratio for this mineral was apparent, while Mlle. Gleditsch[2] reported, for a sample of Colorado carnotite, a ratio of only 2.34×10^{-7}, which corresponds to about 70% of normal ratio. Marckwald and Russell[2] found 91.6% of normal ratio for a carnotite of Colorado and 71.5% for one of Florida(?). From these results the impression seems to have been general that carnotite always has a *low* ratio.

The increasing importance of carnotite as one of the chief sources of radium has made it appear desirable to undertake a thorough examination of the radium : uranium ratio in a much larger number of samples of this mineral. To this end about twenty specimens of carnotite of all grades and from various localities have been examined. By way of anticipation, it may be stated here that, on *small* samples, we have confirmed in some cases the low ratios, finding one almost as low as that of Mlle. Gleditsch, which is to be regarded, however, as very exceptional. On the other hand, we have also found an equal number of *high* ratios (also in the case of small samples only), some as high as the highest ratios found by Mlle. Gleditsch for any of the primary minerals and one considerably higher, 4.6×10^{-7}, which is the highest ratio yet reported for any uranium mineral.

What appears to us to be of the greatest significance is the fact that these abnormal ratios, both high and low, occur only in samples representative of small quantities of ore (a few pounds), while all samples from large lots (1 ton up to a carload) invariably show a ratio practically identical with that of pitchblende. This appears to us to suggest strongly a theory of transposition within the ore bed rather than one of complete removal by leaching. This point will be more fully discussed in the Conclusion; but it is quite evident that there is no reason to suppose carnotite to be abnormal in ratio, provided the determination be made on a sample representative of a considerable portion of an ore bed, while rather large deviations in both directions are found by the examination of small samples.

II. Carnotite Samples.

The samples of carnotite investigated have been chosen with the object of representing the principal localities in Colorado and Utah where this ore has been found in any quantities of importance. All grades of carnotite from 1.5 to 33% of U_3O_8 have been included.

The samples were not collected by the authors, nor were they taken with any reference to geological conditions or position in ore beds but are

[1] Stefan Meyer, *Ibid.*, 122 (June, 1913).
[2] *Loc. cit.*

simply representative of carnotites as they come on the market either as specimens or in commercial quantities. As already mentioned, a special significance attaches to the specimens representative of large quantities of ore. Owing to the magnitude of the present production of carnotite ore we have been fortunate in obtaining ground samples representing large quantities of carefully sampled ore which we feel is of the utmost importance in obtaining correct values for radium content. We wish to take this opportunity of thanking all the gentlemen through whose courtesies we have been supplied with these samples. `

III. General Discussion of Methods.

Two distinct determinations enter into the radium:uranium ratio which contribute equally to the accuracy of the result. The methods of determining radium in carnotite differ little from those employed for many other uranium ores and present no especial difficulties, provided suitable methods are used to liberate the emanation. We have employed the emanation method exclusively and always after attainment of equilibrium in the samples, sealed in glass tubes for a month or more; accumulation methods starting from zero emanation have not been used. Aluminium leaf electroscopes of the Wilson type were used with discharg' chamber and leaf system separate. Calibration was made by means of analyzed pitchblende from Colorado assuming the ratio found by Heimann and Marckwald[1] of 3.328×10^{-7} to be correct.

The determination of uranium in carnotite does present, however, exceptional difficulties owing to the presence of vanadium, and many of the earlier proposed methods of separation have been found unsuitable. Full details of the method which we have found satisfactory are given in Section VII as well as references to other methods which we have employed in some cases for control.

The low uranium content of most carnotites as compared with other higher grade ores renders it difficult to attain the desired degree of accuracy in determining the uranium and, to a less extent, the radium content.   We have sought to overcome this difficulty by repeating determinations frequently and by employing additional methods of control in all cases of doubt. These same precautions have also been used in the radium determinations, which have all been checked by two independent methods of liberating the radium emanation. Especial care has been taken in the case of all abnormal ratios to be sure that the deviations were real ones and not due to errors in the measurement either of radium or uranium. We believe that the average results reported in Sections VIII and IX are accurate to within $1-2\%$.

[1] *Loc cit*

IV. The Emanating Power of Carnotite.

The term "emanating power" was used first by Boltwood[1] to signify the percentage loss of emanation from a radioactive ore, and was applied by him in the determination of radium as an additive correction to the quantity of emanation liberated by direct solution. The emanating power for many samples of carnotite has been found surprisingly large in the present investigation (compare Table IV, Col. 6) varying from 16 to 50%. This high degree of emanating power is not only to be noted as one of the distinguishing characteristics of carnotite but has also formed such a controlling factor in the experimental procedure that it deserves some preliminary attention.

The loss of emanation by the ore is due to a diffusion of the gas and is much lower (only 3 to 8%) in the case of dense, compact minerals like pitchblende than for carnotites which have a looser mechanical structure. For a given sample it is doubtless, as suggested by Rutherford,[2] dependent on the degree of fineness of the ore. We have not undertaken any direct investigation of the relation between emanating power and fineness, or any other property, but have ascertained that fineness cannot be the principal controlling factor among different specimens, as there is no relation whatever apparent between the order of fineness of different samples and their emanating power.

Evidently a given percentage error, in determining the emanating power to be used additively in obtaining the total emanation according to Boltwood, would more seriously influence the final result in case of a carnotite than in an ore where its relative value is small. Our earlier results showed on repetition considerable deviations in emanating power, which suggested that the emanation was not always removed to the same degree from the same sample. This is probably due to differences in the amount of air passed over the ore, or differences in air pressure or velocity, resulting in drawing varying amounts of emanation out of a more or less porous structure. A simple remedy suggested itself as a modification of the Boltwood method, namely, to make the determinations of the emanating power and the emanation liberated by solution strictly complementary to each other, in the sense that each sample dissolved should represent part or the whole of the sample from which emanation had just been drawn to determine the emanating power. By this procedure it is indifferent whether various determinations of emanating power are concordant or not so long as the sums obtained by adding corresponding determinations are in agreement with each other. That the latter is in reality the case may be seen from Table I, in which it will be noted that, for each ore, the agreement for the total emanation is better than that of either of the in- `

[1] *Loc. cit.*

[2] Rutherford, "Radioactive Substances and Their Radiations," p. 364 (1913).

dividual values going to make up the sum. Only a few examples can be given in the table illustrative of this point, because it was soon found more convenient to determine the total emanation in one operation, as will be described below.

TABLE I —ILLUSTRATING ADVANTAGE OF "COMPLEMENTARY" EMANATION METHOD

Ore No [1]	Eman power in curies × 10⁹	+	Soln eman in curies × 10⁹	=	Total eman in curies × 10⁹ per 1 g ore
2	15 0		87 1		102 1
	17 6		84 5		102 1
4	14 0		58 6		72 6
	11 7		60 8		72 5
5	21 8		27 7		49 5
	23 6		26 2		49 8
8	4 38		8 93		13 3
	4 45		8 50		13 0

Unless one desires to know the emanating power itself, it is simpler to determine the total emanation in one operation by sealing the ore in a very thin bulb, of the type shown in Fig 1, for a month or more before breaking under acid to liberate the total emanation

This method checks excellently with the "complementary" modified Boltwood method, as will be seen from Table II. The bulb (a), of 4 to

TABLE II —COMPARING RESULTS OF "SEALED BULB METHOD" (I) FOR TOTAL EMANATION IN ONE OPERATION, WITH "COMPLEMENTARY METHOD" (II)

Ore No		Eman power in curies × 10⁹	+	Soln eman in curies × 10⁹	=	Total eman in curies × 10⁹.
14	I					11 09
	II	3 906		7 188		11 09
15	I					8 08
	II	3 488		4 467		7 96
16	I					7 08
	II	3 191		3 916		7 11
18	I					7 34
	II	1 224		6 156		7 38
19	I					8 54
	II	2 993		5 606		8 60
20	I					29 91
	II	9 847		19 77		29 62
21	I					23 61
	II	10 72		13 12		23 84
22	I					21 21
	II	3 445		17 64		21 09

10 mm. diameter, according to the quantity of ore to be used, is blown very thin so as to break without endangering the outer flask (f) containing HNO₃. The weighed ore is introduced into the bulb through (b) and then

[1] This numbering of samples is the same as used throughout the paper See Section VIII

the glass stem (c) is sealed on and constricted to make a complete seal at (d) the upper end (e) being also sealed for convenience The whole is introduced through a double-bored rubber stopper (g) just off the bottom of the flask (f) and may be broken by a slight downward rap on (e) By boiling the acid the ore is readily attacked and all of the emanation is boiled over into a gas buret (compare Fig 11) The good agreement between this method and the one already described may be seen from Table II

Fig. 1
Emanation Method
Using Sealed Tube

In connection with fusion methods to be later described, it was of interest to know the emanating power of the cold solidified mass resulting from the fusion of carnotite in sodium carbonate On investigation its emanating power proved to be zero, which is in marked contrast with the action of carnotite in the cold without flux Since we have always found (compare Table III) great difficulty in removing emanation even out of the hot fusion of carnotite in Na_2CO_3-K_2CO_3 mixture, although the same method works well on pitchblende or crude sulfates, the following suggested itself to us   If the cold fusion loses no emanation, while the ore alone loses large percentages, it seemed plausible that a direct ignition of the ore with no flux might bring about the liberation of emanation more readily than with a flux This procedure proved eminently successful with carnotite (though a complete failure for crude sulfates) and has served in all cases as a control for the solution method

Impracticability of Solid Radiation Methods for Carnotite —It should also be noted while dealing with emanating power that the high and variable values exhibited by carnotite seem to preclude the possibility of employing, for accurate determination, any radiation method from the solid ore for either alpha, beta, or gamma rays, unless, in the employment of the gamma-ray method, a large quantity of ore could be kept for a month and then measured in an absolutely tight vessel

V. Emanation Method for the Determination of Radium.

For the liberation of emanation from carnotite we originally proposed to employ three methods   (1) Solution in boiling 1–1 HNO_3 (a) corrected for "emanating power" by the "complementary" method already de-

scribed in Section IV; (b) by a single operation, by dissolving ore in equilibrium with emanation from a sealed tube. By reference to Table II it will be seen that both modifications of this method are equally suitable. (2) Fusion with a Na_2CO_3-K_2CO_3 mixture, which is later fused again in a Jena glass tube. This method will be seen from Table III to give very low results for carnotite and was soon abandoned. Perhaps by means of electrical heating to a higher temperature the emanation could be expelled from the fusion. The heating employed, both here and for the direct ignition method, was by means of a Méker burner. A Jena glass tube, into which the ore or fusion is introduced directly (without boat) and held in place by glass wool plugs, was held in the bare flame of this burner. (3) Direct ignition of the ore under conditions just described This method was suggested by the high emanating power of carnotite and has proved entirely satisfactory, giving results which accord well with those of the solution method (cf. Table III).

In the solution method the emanation always was allowed to stand in a gas buret for ten minutes before passing into the electroscope, to allow any possible thorium emanation to decay; while in the ignition method air was passed directly over the heated ore through a small H_2SO_4 drying bulb into the exhausted electroscope The fact that both methods give concordant results indicates the absence of thorium in carnotite. This is further supported by the return of the natural leaks of the electroscopes after a few hours to their original values, which would not be the case for the induced activity of thorium. (4) Fusion with Na_2CO_3-K_2CO_3 followed by solution in 5% Na_2CO_3, filtration, solution of the residue in 1–3HNO_3, and subsequent boiling off of both alkaline and acid solutions. This method, which is referred to as the *fusion and solution* method in Table III, will be seen to give results about 10–20% low. This we attribute to the almost invariable precipitation of some colloidal silica, involving the adsorption of radium and consequent loss of some emanation.

Of the four methods tried, two were found suitable and two unsuitable, as will be seen from the comparative results in Table III.

TABLE III —COMPARATIVE RESULTS OF DIFFERENT METHODS FOR DE-EMANATING CARNOTITES

	Total emanation in curies $\times 10^9$ by method			
Ore No	(1) Solution in 1–1HNO_3	(2) Fusion with Na_2-K_2CO_3	(3) Ignition	(4) Fusion and solution
2 . ..	101 4	63 5	98 0	83 0
4	72 6		73 3	53.8
13	7 83	2 62	7 89	6 20
14	11 09		11 63	8 92
15	8 08			6 98
16 .	7 11		7 17	
17 . ..	8 66		8 65	7 38

Solution and Boiling off the Emanation requires no especial explanation. The apparatus is shown in Fig. 11.

Hot water containing some NaOH is used in the gas buret (*h*); $1-1HNO_3$ is used as solvent in flask (*f*). A glass stopcock at (*s*) has been found more convenient than rubber tubing and a clamp.

Fig 2
Apparatus for
Dissolving Carnotite
and
Collecting the Emanation

All possibility of loss of emanation by the passage of water into the side arm (*t*) is avoided by allowing all air to pass up into (*h*) before the bulb (*a*) is broken. In case of an ore not sealed in glass, the same may be accomplished by folding a filter paper containing ore, so that it remains in the neck of flask (*f*) until all air is expelled and the steam softens the paper, allowing it to drop into the acid. The stopcock should be closed at this time, or on breaking the glass bulb, and then gradually opened to prevent a sudden rush of gas from carrying undissolved ore up into the alkali. Pitchblende used for standardization purposes was treated in the same way as carnotite, either directly with correction for emanating power or from a glass tube which had been sealed one month.

For the ignition method the ore was sealed in a straight piece of Jena combustion tubing drawn down to capillary points at both ends. The tubes were about 4 to 10 mm. internal diameter, depending upon the volume of the sample, and about 15 to 20 cm. long. The weighed ore was introduced through one end, which was then drawn out and sealed. The ore is held in place in the middle portion of the tube by means of glass wool plugs. After standing one month or more the tube was connected through H_2SO_4 micro-drying bulbs (cf. Fig. 2*a*) to the exhausted electroscope on one side and to the outside air on the other side. After breaking the capillary ends inside the rubber connections, air was allowed to sweep over the ore, the tube being heated by a Méker burner ($1^1/_{16}$ inch grating) until the Jena glass completely collapsed. This treatment will be seen, by reference to Table III, to give complete de-emanation.

VI. The Electroscope Measurements.

Two electroscopes were employed, both of the Wilson type, with sulfur insulation between the leaf chamber and the ionization chamber below. The volumes of the latter were about 1 and $1/_2$ liter, respectively, the former cubical and the latter cylindrical in shape.

Perhaps because of the symmetrical shape of the ionization chambers it appeared to make little difference whether equilibrium with induced activity was attained with or without a charge on the instrument   Consequently, after allowing the gas to remain in the electroscope for three hours, a charge was put on for 10 to 15 minutes before taking a series of ten readings over 40 scale divisions   Quantities of emanation were usually introduced such as to give a discharge of about 1 division per second

Fig 2a
H_2SO_4 Micro drying
Tube

Standardization was carried out by dissolving about 40 mg of carefully analyzed (cf Sections VIII and XII) pitchblende of Colorado in boiling 1 1HNO₃, assuming the Ra/U ratio as 3 328 ∨ 10 ⁷ according to Heimann and Marckwald [1] The analysis of pitch blende was carried out by the method employed for carnotite (cf Section VII), with the omission of the procedure for the separation of vanadium

Data for Standard Pitchblende — One gram of standard pitchblende contains 0 765 g U_3O_8 = 0 649 g U = 2 16 × 10^{-7} g radium   Emanating power = 2 7%   Therefore, 1 mg dissolved directly gives 2 10 × 0⁻ ¹⁰ curies of radium emanation

As a control of standardization of the electroscopes before each de termination a gamma-ray measurement was carried out by placing a sealed glass tube, containing about 1 mg of radium element in a tube fixed to the base of the discharge chamber, and measuring the rate of the discharge produced, which usually remained practically constant   Deviations of 2 to 3%, attributable to variations in pressure and temperature of the air, were used as direct corrections instead of the usual barometric and tem perature corrections   Deviations greater than 2 or 3% were attributed to changes in the leaf system, necessitating recalibration   New calibrations were not found necessary oftener than in 1 to 2 months

Emanation was introduced into the partially exhausted chamber through a micro drying tube filled with H_2SO_4 (cf Fig 2a), any possible spray from which was prevented from entering the chamber by a short layer of cotton batting   After using the electroscope, the emanation was immediately removed by a current of dry air taken from outside the laboratory and the natural leak of the instrument determined the following day, before use

VII. The Determination of Uranium.

The method which we have found most satisfactory for the determination of uranium in carnotite is a gravimetric one given below in full detail, including the volumetric determination of vanadium   Although having
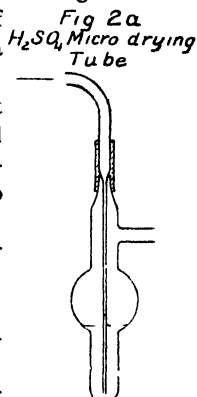
[1] *Loc cit*

no direct bearing on the present subject we include in Section VIII the data for vanadium in order to illustrate its occurrence in typical carnotites.

Gravimetric Method for Vanadium and Uranium in Carnotite[1] *and Other Ores.*—Treat from 2–5 g. of ore, according to the amount of V, Fe, and U present, in a covered beaker, with 10 cc. HCl and let it stand fifteen minutes with occasional shaking. Add 5 cc. HNO_3 and heat on a steam bath. When quiet, remove the cover and evaporate to dryness. Add 3 cc. HCl and 5 cc. H_2O to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 cc. hot water, filter into a small beaker and wash the residue with warm water.

Some ores do not yield all the V to this treatment; a little of it may remain with the insoluble residue. To make sure that all V is in solution ignite the residue in a platinum dish, treat it with 5 cc. of HF and evaporate to dryness on a steam bath. Do not bake the residue. It is not necessary to expel all SiO_2. Add 3 cc. of HCl to the residue from the HF treatment, and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat the residue with 2 cc. of HCl and 2 cc. H_2O and manipulate until any red crust is dissolved, dilute the solution with water and filter it into the main liquid.

Pass H_2S into the liquid to separate copper, etc., filter and boil the liquid to expel H_2S. Concentrate the liquid to 100 cc. if necessary, and oxidize it with an excess of H_2O_2 and then neutralize with dry Na_2CO_3, adding 2 or 3 g. in excess. Boil the liquid for about fifteen minutes, until the yellowish U precipitate dissolves, leaving a brown precipitate which is principally iron. Filter and wash the iron precipitate with water, reserving the filtrate. Dissolve the iron precipitate in the least possible amount of HNO_3 (1–1), and add 10 cc. of H_2O_2, neutralize with Na_2CO_3, add an excess of 2 g. and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain a little V—reserve it for further treatment.

Concentrate the united filtrates from the iron precipitation to a volume of about 200 cc., add 10 cc. of strong HNO_3 and boil until all CO_2 is expelled. Neutralize the free acid with ammonia (until a slight permanent precipitate appears), then add 4 cc. of HNO_3 for each 100 cc. of liquid. Now add 10 cc. of a 20% lead acetate solution, and *enough* (about 20 cc.) of a strong solution of ammonium acetate to reduce the hydrogen ion concentration approximately to that of acetic acid. The object is to precipitate the V as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 cc. of strong ammonia, 100 cc. of water and 70 cc. of 99% acetic acid.

Heat the liquid containing the lead vanadate precipitate on the steam bath for one hour or more, filter on a tight filter and wash with warm water.

[1] Cf. U. S. Bureau of Mines, *Bulletin* 70, by R. B. Moore and K. L. Kithil, p 88.

Dissolve the precipitate in the least possible quantity of hot *dilute* (not stronger than 1-3) nitric acid, neutralize as before, add 3 cc. of HNO_3 in excess, add 2 cc. of lead acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the *filtrate* to the first one.   Reserve the precipitate of lead vanadate for treatment described below.   Concentrate the united filtrates from the lead vanadate to about 400 cc., add 10 cc. of strong H_2SO_4 to separate the bulk of the lead (derived from the excess of lead acetate) as $PbSO_4$, filter it off and wash with cold H_2O.   Neutralize the filtrate from the $PbSO_4$ with ammonia and add *freshly prepared* $(NH_4)HS$ until the solution is yellow and the uranium and what little lead is present are separated as sulfides.   Warm the mixture on a steam bath until the sulfides settle well. Filter and wash *slightly* with warm water.

Dissolve the ppt. with hot dilute nitric acid (1-2) and collect the solution in a No. 2 beaker, add 5 cc. of H_2SO_4 and evaporate to the appearance of fumes, cool and take up with water, boil and let the small amount of $PbSO_4$ settle until the solution is cold, filter it off and wash it with very little dilute H_2SO_4.

Separation of Alumina.—Nearly neutralize the filtrate with ammonia; have the solutions cool (not over 30°) and add powdered carbonate of ammonia in about 2 g. excess, let the precipitate of alumina settle, filter it off, wash with warm water and if it appears to be a considerable amount, or is at all yellow in color, dissolve it in a little dilute H_2SO_4 and reprecipitate with ammonium carbonate as above.   Acidulate the filtrate from the alumina with H_2SO_4, boil thoroughly to expel CO_2, make the liquid slightly alkaline with NH_4OH while it is hot and heat on the water bath until the ammonium uranate collects and settles.   Filter and wash with very dilute $(NH_4)NO_3$ (2%).   Do not allow the precipitate to run dry on the filter after the first washing.   Dry the precipitate and ignite it in porcelain, weighing as U_3O_8.   Dissolve the precipitate in HNO_3 and test it with H_2O_2 for vanadium and with $(NH_4)_2CO_3$ for aluminium.

Dissolve the lead vanadate in dilute nitric acid, add 10 cc. of H_2SO_4 and evaporate the mixture until fumes appear.   Cool, take up with water, and add fusion solution (see following paragraph), add 10 cc. of concentrated solution of SO_2 to the mixture, boil until the excess of SO_2 is expelled and titrate the hot solution with potassium permanganate solution.   The reduction of the solution by SO_2 is from V_2O_5 to V_2O_4.   It is not necessary to filter out the lead sulfate before boiling to expel SO_2.   The boiling is best done in a large flask.   In expelling the excess of SO_2, it is necessary to boil the liquid for at least ten minutes after the odor of SO_2 can no longer be detected.

The iron precipitate, which was produced by the addition of Na_2CO_3 and H_2O_2 to the original acid solution, may contain vanadium.   Ignite

it in a platinum crucible and fuse it with Na_2CO_3, leach the fusion with water, filter, acidulate the filtrate with H_2SO_4 and add it to the main solution before reducing with SO_2 or reduce and titrate it separately if preferred.

For the details of other methods of control one is referred to *Bulletin* 70, of the Bureau of Mines, 1913 and 1914, pp. 82 to 91.

In general, it may be stated that the most prevalent errors in the determination of uranium result in the precipitation of some other material, such as SiO_2, Al_2O_3, or V_2O_5, along with uranium, which would produce a low Ra/U ratio. To guard against the former two possibilities, we have usually redissolved U_3O_8 and passed the solution through a Jones' reductor to determine uranium volumetrically by titration with $KMnO_4$.

VIII. Experimental Data for Carnotites.

No 1.[1] A sample from 65 lbs, Cripple Creek claim Long Park, Paradox Valley, Colorado Per cent U_3O_8 2 10, 2 08, 2 12, Av *2 095 = 1 78%* U Av per cent V_2O_5, 2 53 Ra per g $\times$ 10⁹ 5 94,[2] 6 11, and 5 99 (ignition method) Av *6 02 $\times$ 10⁻⁹ g* Em power = 29 6% Ra/U = *3 38 $\times$ 10⁻⁷*

No 2. A small sample from the "Rajah" claim, Roc Creek, Paradox Valley, Colorado Per cent U_3O_8 33 19, 33 24, Av *33 22 = 28 18%* U Av per cent V_2O_5, 14 05 Ra per g $\times$ 10⁸ 1 50 + 8 71 = 10 21, 1 67 + 8 34 = 10 01, 1 76 + 8 44 = 10 20, Av *10 14 $\times$ 10⁻⁸ g* Em power = 16 2% Ra U − *3 59 $\times$ 10⁻⁷*

No 3. A small sample from "Black Fox" claim, Bull Canon, south of Paradox Valley, Colorado Per cent U_3O_8 1 63, 1 57, 1 60, 1 58, Av *1 595 = 1 35%* U Av per cent V_2O_5, 5 22 Ra per g $\times$ 10⁹ 2 15 + 2 06 = 4 21, 4 29, 4 30, 4 23 (ignition), Av *4 26 $\times$ 10⁻⁹ g* Em power = 50 5% Ra/U = *3 10 $\times$ 10⁻⁷*

No 4. A small sample from "Florence" claim, Long Park, Paradox Valley Colorado Per cent U_3O_8 23 54, 23 42, Av *23 48 = 19 92%* U Av per cent V_2O_5, 10 63 Ra per g $\times$ 10⁸ 1 404 + 5 861 = 7 27, 1 166 + 6 082 = 7 25, 7 33 (ignition) Av *7 28 $\times$ 10⁻⁸ g* Em power 17 7% Ra/U = *3 66 $\times$ 10⁻⁷*

No 5. Small sample from a Curran claim, Long Park, Paradox Valley, Colorado Per cent U_3O_8 24 03, 23 43, 24 75, 24 37, Av *24 25 = 20 60%* U Av per cent V_2O_5, 13 51 Ra per g $\times$ 10⁸ 2 18 + 2 77 = 4 95, 2 36 + 2 62 = 4 98, 4 95, 4 97 (ignition), Av *4 96 $\times$ 10⁻⁸ g* Em power 45 8% Ra/U = *2 41 $\times$ 10⁻⁷*

No 6. A small sample of a concentrate prepared by a method which may have affected its Ra/U ratio Hence the data of No 6 are not included in Table IV Per cent U_3O_8 9 20, 9 05 Av *9 125 = 7 74%* U Av per cent V_2O_5, 10 08 Ra per g $\times$ 10⁸ 2 166, 2 167, 2 184 (ignition), Av *2 17 $\times$ 10⁻⁸ g* Em power = 30 4% Ra/U = *2 80 $\times$ 10⁻⁷*

No 7. Small sample from "Florence" claim, Long Park, Paradox Valley, Colorado Per cent U_3O_8 3 16, 3 17, 3 23, 3 19, Av *3 185 = 2 70%* U Av per cent V_2O_5, 4 82 Ra per g $\times$ 10⁹ 4 26 + 6 35 = 10 61, 10 86, 10 58 and 10 60, 10 94 (ignition), Av *10 72 $\times$ 10⁻⁹ g* Em power = 39 7% Ra/U = *3 97 $\times$ 10⁻⁷*

No 8. Sample of 3,016 lbs from a Cummings claim, Bull Canon, south of Paradox Valley, Colorado Per cent U_3O_8 4 78, 4 72, 4 62, 4 61 Av *4 68 = 3 97%*

[1] The order of numbering is one of convenience only, but the same numbers have been used for the same ores throughout the paper

[2] Ra values consisting of the sum of two determinations refer to the "complementary" method, those without designation refer to method of total emanation by solution in one operation; ignition methods are designated as such.

U   Av per cent V_2O_5, 4 10   Ra per g × 10^9 4 38 + 8 93 = 13 31, 4 45 + 8 50 = 12 95, 12 42, 12 90 (ignition), 13 67, Av $13\ 05$ × 10^{-9} g   Em power = 33 9% Ra/U = $3\ 29$ × 10^{-7}

No 9.   Sample of 29,118 lbs from same locality as No 8   Per cent U_3O_8 1 52, 1 57 1 48   Av $1\ 523$ = $1\ 29$% U   Av per cent V_2O_5, 4 00   Ra per g × 10^9 1 052 + 3 294 = 4 35, 0 719 + 3 500 = 4 22, 4 43 4 41 (ignition)   Av $4\ 35$ × 10^{-9} g   Em power = 20 4%   Ra/U = $3\ 42$ × 10^{-7}

No 10.   Sample of about 4 000 lbs from same location as No 5   Per cent U_3O_8 2 45 2 35, 2 48   Av $2\ 40$ = $2\ 04$% U   Av per cent V_2O_5 5 27   Ra per g × 10^9 7 23, 7 40, 7 30 (ignition)   Av $7\ 31$ × 10^{-9} g   Em power = 29 0% Ra/U = $3\ 58$ × 10^{-7}

No 11.   Small sample from Melrose claim, Green River District Utah   Per cent U_3O_8 4 14 4 11 4 12 4 16   Av $4\ 13$ = $3\ 50$% U   Av per cent V_2O_5 5 07 Ra per g × 10^9 4 83 + 5 74 = 10 57' 5 05 + 5 73 = 10 78, 11 12 10 87 (ignition) 11 41   Av $10\ 95$ × 10^{-9} g   Em power = 45 1%   Ra/U = $3\ 13$ × 10^{-7}

[No 12.   (Standard) Pitchblende from Kirk Mine, Gilpin Co, Colorado   Per cent U_3O_8 76 40, 76 58   Av $76\ 50$ = $64\ 9$% U   Ra per g 2 16 × 10^{-7} (calculated from Heimann and Marckwald's[1] Ra/U ratio $3\ 328$ × 10^{-7}, also in close agreement with a sample of analyzed pitchblende of known radium content from Boltwood) Em power 2 7% by two determinations of 5 98 and 5 73 × 10^{-9} curies respectively]

No 13.   Sample of a carload lot (ca 30 tons) from the claims of the Crucible Steel Co, Long Park, Colorado   Per cent U_3O_8 2 74, 2 82   Av $2\ 78$ = $2\ 36$% U Av per cent V_2O_5, 4 67   Ra per g × 10^9 3 51 + 4 32 = 7 83, (ignition), 7 89 Av $7\ 86$ × 10^{-9} g   Em power = 44 7%   Ra/U = $3\ 34$ × 10^{-7}

No 14.   Sample of carload lot (ca 25 tons) from the same locality as No 13 Per cent U_3O_8 3 91, 3 95   Av $3\ 93$ = $3\ 33$% U   Av per cent V_2O_5 5 12   Ra per g × 10^9 3 90 + 7 19 = 11,09, 11 09   Av $11\ 09$ × 10^{-9} g   Em power = 35 2% Ra/U = $3\ 33$ × 10^{-7}

No 15.   Sample of a carload lot (ca 20 tons) from same locality as No 13   Per cent U_3O_8 2 85, 2 82, Av $2\ 835$ = $2\ 41$% U   Av per cent V_2O_5, 4 72   Ra per g × 10^9 3 488 + 4 467 = 7 955, 8 076, Av $8\ 02$ × 10^{-9} g   Em power = 43 4%   Ra/U = $3\ 33$ × 10^{-7}

No 16.   Sample of a carload lot (ca 22 tons) from some locality as No 13   Per cent U_3O_8 2 52, 2 54, Av $2\ 53$ = $2\ 16$% U   Av per cent V_2O_5, 3 75   Ra per g × 10^9 3 191 + 3 916 = 7 107, 7 077 (ignition) 7 219, 7 174, Av $7\ 14$ × 10^{-9} g Em power = 44 9%   Ra/U = $3\ 32$ × 10^{-7}

No 17.   Sample of a carload lot (ca 19 tons) from same locality as No 13   Per cent U_3O_8 3 05, 3 03, 3 06, Av $3\ 05$ = $2\ 59$% U   Av per cent V_2O_5 4 66   Ra per g × 10^9 8 66, 8 65 (ignition)   Av $8\ 66$ × 10^{-9} g   Em power = 47 7% Ra/U = $3\ 34$ × 10^{-7}

No 18.   Small sample from Kelly Lode No 3, west of McIntyre District Colorado, near Utah boundary   Per cent U_3O_8 25 63, 25 71, Av $25\ 67$ = $21\ 77$% U   Av. per cent V_2O_5, 22 3   Ra per g × 10^8 1 224 + 6 156 = 7 38, 7 34, 7 37 (ignition) Av $7\ 36$ × 10^{-8} g   Em power = 16 6%   Ra/U = $3\ 38$ × 10^{-7}

No 19.   About 60 lbs of a composite sample of several ores   Per cent U_3O_8 3 18, 3 26, 3 17, 3 10, Av $3\ 18$ = $2\ 70$% U   Av per cent V_2O_5, 4 03   Ra per g × 10^9 (ignition) 8 902, 8 935, Av $8\ 92$ × 10^{-9} g   Em power = 33 5%   Ra/U = $3\ 30$ × 10^{-7}

No 20.   A small sample from Horse Mt, Eagle County, Colorado   Per cent. U_3O_8 7 81, 7 75, Av $7\ 78$ = $6\ 60$% U   Av per cent V_2O_5, 8 80   Ra per g × 10^9

[1] *Loc cit*

9 85 + 19 77 = 29 62, 29 91,'30 62 (ignition) 30 98　Av *30 3* × *10⁻⁸* g　Em power
= 29 6%　Ra/U = *4 59* × *10⁻⁷*

No 21.　A small sample from a Meyer's claim, South Park, Colorado　Per cent
U_3O_8 9 52, 9 20, Av *9 36* = *7 94*% U　Av per cent V_2O_5, 3 85　Ra per g　× 10⁸
1 07 ⌐ 1 31 = 2 38, 2 36, 2 37 (ignition)　Av *2 37* × *10⁻⁸* g　Em power = 45 2%
Ra/U = *2 99* × *10⁻⁷*

' No 22.　A lot of several hundred pounds from the Wade and Taylor claims, Pac
Creek, near Moab, Utah　Per cent U_3O_8 *7 52* = *6 38*% U　Av per cent V_2O_5
11 23　Ra per g　× 10⁸ 0 344 + 1 764 = 2 11, 2 12 (ignition) 2 15　Av *2.13* ×
10⁻⁸ g　Em power = 16 2%　Ra/U = *3 34* × *10⁻⁷*

No 23.　Sample of 1,120 lbs 'from the same locality as No 22　Per cent U_3O_8
11 62 = *9 86*% U　Ra per g　× 10⁸ 3 29, 3 26 (ignition)　Av *3 28* × *10⁻⁸* g
Em power = 25 1%　Ra/U = *3 33* × *10⁻⁷*

No 24.　Sample of about one ton of ore of unknown origin, very finely ground
suspected of being a mill product from which radium had been largely removed, and
mixed with a low grade carnotite　Per cent U_3O_8 8 83, 8 85　Av *8 84* = *7 50*% U
Av per cent V_2O_5 6 87　Ra per g　× 10⁸ 3 99, 3 88 4 24 (ignition)　Av *4 04* ×
10⁻⁸ g　Ra/U = *0 54* × *10⁻⁷*

NOTE —The reasons for distrusting this sample as not being a natural carnotite
ore are rather numerous　Its Ra/U ratio is very abnormally low its origin could not

TABLE IV —SUMMARY OF EXPERIMENTAL DATA FOR CARNOTITES

Ore No	Locality [1]	% U_3O_8	% U	G Ra × 10⁹ per 1 g ore	Emanating power in %	Ra/U × 10⁷	% normal ratio (pitch blende = 100%)
5	Paradox Valley	24 25	20 6	49 6	45 8	2 41	72 4
21	South Park	9 36	7 94	23 7	45 2	2 99	89 8
11	Green River, Utah	4 13	3 50	10 95	45 1	3 13	94 0
3	South of Paradox	1 60	1 35	4 26	50 5	3 16	94 9
8	South of Paradox	4 68	3 97	13 05	33 9	3 29	98 8*
19	(A mixture)	3 18	2 70	8 92	33 5	3 30	99 1
16	Long Park	2 53	2 16	7 14	44 9	3 32	99 7*
14	Long Park	3 93	3 33	11 09	35 2	3 33	100 0*
15	Long Park	2 84	2 41	8 02	43 4	3 33	100 0*
23	Moab, Utah	11 62	9 86	32 8	25 1	3 33	100 0*
13	Long Park	2 78	2 36	7 86	44 7	3 34	100 3*
17	Long Park	3 05	2 59	8 66	47 7	3 34	100 3*
22	Moab Utah	7 52	6 38	21 3	16 2	3 34	100 3*
18	McIntyre District	25 67	21 77	73 6	16 6	3 38	101 5
1	Long Park	2 10	1 78	6 02	29 6	3 38	101 5
9	South of Paradox	1 52	1 29	4 35	20 4	3 42	102 7*
10	Paradox Valley	2 40	2 04	7 31	29 0	3 58	107 5*
2	Paradox Valley	33 22	28 18	101 4	16 2	3 59	107 8
4	Long Park	23 48	19 92	72 8	17 7	3 66	109 9
7	Long Park	3 19	2 70	10 72	39 7	3 97	119 2
20	Eagle County	7 78	6 60	30 3	29 6	4 59	137 8

Av , 101 8

[1] In Colorado when not otherwise specified　See preceding sections for fuller de-
tails

* All samples starred represent large quantities of ore (several hundred pounds up
to 25 tons).

be ascertained. Examined under the microscope, it appears full of a net work of crystalline needles partly soluble in water (apparently $CaSO_4$), such as could not have existed in the original ore because the length of the crystals is several times the average diameter of other particles, showing that they must have formed after the ore was ground. On ignition, considerable quantities of sulfur are distilled off, probably owing to reduction of sulfates by organic matter. For these reasons we have not regarded it as natural carnotite, and have presented the data for whatever general interest they may have, without including them in Table IV, however.

IX. Discussion of Results.

On inspecting the last two columns of Table IV, there appears to be only one possible conclusion as to the radium : uranium ratio of carnotite; namely, that it is identical with that of pitchblende in all large quantities of well-sampled ore. This appears, in general, to be true regardless of the locality or composition of the ore. The *low* and *high* ratios occur only in cases of small samples and are apparently due to local transposition of radium within the ore bed, resulting in differences which are completely equalized on sampling sufficient quantities of ore. We are not prepared to go further into the nature of this transposition at the present time, because, as already stated, the samples were not collected with this object in view.

Of course, the fact that the average of all ratios in Table IV should be within 2% of normal is somewhat accidental; but that the average of all the large samples is within 1% of normal appears by no means accidental and seems to represent about the average of our limits of experimental error.

The question naturally presents itself as to whether high and low ratios for other minerals can be explained in the same way as for carnotite. As far as the authors are aware, it is true that determinations of the radium :-uranium ratio have been made in all the minerals examined on small samples only. On the other hand, it is to be recalled that high ratios had not been hitherto reported except in the case of primary minerals which are not so much subject to the action of water. Furthermore, in the case of autunite, where leaching certainly does produce very low ratios, no high ratios have ever been found to support the view of "transposition" as put forward for carnotite. In such instances it has been found that the leaching process removes the radium completely from association with the original uranium parent, usually disseminating it very widely, or in exceptional cases forming deposits containing considerable radium with no uranium, as found by Jacques Danne[1] in a specimen of pyromorphite at Issy L'Eveque.

The difference in the completeness of leaching exhibited by autunite and carnotite may be due to the fact that the latter occurs in a region of very low rainfall; in fact, aridity seems to be a necessary condition for the

[1] Jacques Danne, *Compt. rend.*, **140,** 241 (1905).

existence of carnotite. Under such conditions and in view of the fact that the extent of carnotite deposits is frequently quite large, a "transposition" of radium might be expected rather than a complete removal.

The high degree to which carnotite gives up its emanation by diffusion as shown in Table IV and discussed in Section IV, appears rather remarkable. This property does not seem to be connected with any other known properties of the ores and we are not able at present to do more than call attention to it, as well as to note that carnotite appears to furnish, in the solid state, a more abundant source of radium emanation than any other mineral with the same radium content.

X. Summary.

1. Samples of carnotite representing large quantities of ore (a few hundred pounds to several tons) show a Ra/U ratio identical with that of pitchblende, 3.33×10^{-7}.

2. Samples from small quantities (a few pounds) tend to exhibit abnormal Ra/U ratios. One instance as low as 2.48×10^{-7} and one as high as 4.6×10^{-7} have been found.

3. The most plausible explanation for these ratios seems to be one of "transposition" of radium within an ore bed, producing local differences which are equalized in mixing large quantities of ore.

4. The "emanating power" of carnotite is high and varies from 16 to 50%.

5. In order to obtain concordant results by the Boltwood emanation method, it was found desirable to determine the emanation liberated by solution in the same sample from which the emanating power had just been determined, thus making the two determinations strictly "complementary."

6. Radium may be more easily determined by the emanation method in one operation either by solution or by ignition from tubes in which it has been sealed for one month to reach equilibrium.

7. In contrast with the successful solution or ignition method for de-emanating carnotite, fusion with carbonate, and also the fusion and solution methods both gave low results and were abandoned.

It gives us great pleasure to acknowledge our indebtedness to Professor R. B. Moore for his helpful advice during this investigation.

UNITED STATES BUREAU OF MINES,
          DENVER, COLO.

CESIUM ALUM AND ITS PROPERTIES.

BY EDWARD HART AND HENRY B. HUSELTON.

Since the discovery of cesium by Bunsen, in 1860, its compounds have been investigated at various times, but a broad field for research still

exists. The alum is one of the many compounds of cesium that offer an opportunity for original work.

Cesium alum was studied by Redtenbacher[1] in 1865, by Carl Setterberg[2] in 1881, and by Locke[3] in 1901. Setterberg compared the solubility of rubidium and cesium alums at eight different temperatures. Locke, in his work on an examination of all possible alums, gives the solubility of cesium alum at four temperatures and two of these differ from the results obtained by Setterberg. His other values were found at temperatures not given by Setterberg and, therefore, must be compared with interpolated figures. They are not the same.

The alum used was prepared from pollucite by treatment with sulfuric and hydrofluoric acids, followed by solution in water and recrystallization. The pollucite used appeared to contain zirconium. A considerable amount of jelly-like material separated, probably a zirconium compound, which was not further examined. This renders filtration difficult and tedious. The crude alum had a slight yellow color, due to ferric iron, which was removed by recrystallization from water containing sulfur dioxide.

The crystals finally obtained were examined spectroscopically and found to be free from rubidium and potassium. These crystals were used in the following

TABLE I —SOLUBILITY DETERMINATIONS

No	Temp	Residue per 100 g H_2O Gram	No	Temp.	Residue per 100 g H_2O Grams
1	7°	0 255	10	47°	1 173
2	19	0 422	11	49 25	1 387
3	22	0 426	12	50	1 417
4	22 5	0 435	13	56	1 86
5	24	0 474	14	60	2 06
6	29 5	0 571	15	66	2 798
7	31 5	0 607	16	66	2 85
8	40	0 865	17	68	3 13
9	41	0 879	18	80	5 78

The first five values of Setterberg coincide almost exactly with ours. Above 40° his values are less. In Table II, the values from 0–7° were obtained by interpolation using Setterberg's values for 0°. From 80–100° they were calculated by extrapolation and are only approximately correct.

Specific Gravity.—The specific gravity of the hydrated alum was obtained by weighing in 95% ethyl alcohol in which it is insoluble. Two determinations were made giving 1.96 and 1.93, average 1.945.

Melting Point.—The hydrated crystals in powder were enclosed in the usual capillary tube, which was heated in sulfuric acid. After the alum had

[1] Redtenbacher, *J prakt Chem*, **94**, 442 (1865).

[2] Setterberg, *Ann*, **211**, 100 (1882)

[3] Locke, *Am Chem J*, **36**, 166 (1901)

TABLE II.—THE SOLUBILITY OF ANHYDROUS CESIUM ALUM, $AlCs(SO_4)_2$ IN WATER

Temp.	Grams per 100 g H₂O.	Temp	Grams per 100 g H₂O.	Temp.	Grams per 100 g H₂O.	Temp.	Grams per 100 g H₂O.
0°	0 19	22°	0 43	48°	21	70°	3 50
1	0 20	23	0 45	49	27	71	3 67
2	0 21	24	0 47	50	30	72	3 85
3	0 22	25	0 49[1]	51	39	73	4 07
4	0 23	26	0 50	52	45	74	4 30
5	0 24	27	0 51	53	51	75	4 50
6	0 25	28	0 52	54	58	76	4 72
7	0 26	29	0 55	55	65	77	4 95
8	0 27	30	0 57	56	71	78	5 15
9	0 28	31	0 59	57	77	79	5 40
10	0 29[1]	32	0 60	58	86	80	5 78
11	0 30	33	0 62	59	92	81	6 05
12	0 31	34	0 65	60	2 06	82	6 4
13	0 32	35	0 69[1]	61	2 14	83	6 7
14	0 34	36	0 72	62	2 25	84	7 0
15	0 35	37	0 75	63	2 37	85	7 4
16	0 36	38	0 77	64	2 50	86	7 7
17	0 38[1]	39	0 80	65	2 65	87	8 0
18	0 39	40	0 85	88	8 3	95	10 1
19	0 40	41	0 87	89	8 6	96	10 4
20	0 41	42	0 91	90	8 8	97	10 8
21	0.42	43	0.96				
44	1 01	66	2 78	91	9 0	98	11 1
45	1 06	67	2 96	92	9 2	99	11 5
46	1 10	68	3 13	93	9 5	100	12 0
47	1 17	69	3 34	94	9 9		

NOTE —0° to 40° accurate as given   40° to 80°, first decimal correct   80° to 100°, extrapolated, approximately correct

melted, a fine capillary was inserted and the solidifying point determined by drawing on the capillary until it broke. The following determinations show that the alum melts at 117°.

	Beginning	End	Solid.	Average.
	118°	118°	115°	116 5°
	116	118	117	117
.	117	118	116	117
	———	———	———	———
Average,	117	118	116	117

The melting point of cesium alum has been determined as follows: Tilden,[2] 106°; Erdman,[3] 120.5°; Locke,[4] 122°.

EASTON, PA

[1] Given by Setterberg
[2] Tilden, *J Chem Soc*, **45**, 266 (1884)
[3] Erdman, *Arch Pharm*, **232**, 3.
[4] Locke, *Am Chem J*, **26**, 183 (1901).

THE PERCHLORIC METHOD OF DETERMINING POTASSIUM, AS APPLIED TO WATER ANALYSIS.

By Clarence Scholl.
Received May 4, 1914

Potassium is determined gravimetrically as potassium chloroplatinate (K_2PtCl_6), as potassium cobaltinitrite $(K_3Co(NO_2)_6)$, and as potassium perchlorate $(KClO_4)$.

The potassium chloroplatinate method is most commonly used. It is accurate, but there are difficulties because of the solubility of the salt in alcohol, the non-uniformity of the precipitate, the loss by ignition, and the cost of material. The cost of chloroplatinic acid equivalent to 1 g. of potassium in the precipitate, K_2PtCl_6, amounts to $4.90. While this material can be recovered, the cost of recovery is considerable.

The determination as potassium cobaltinitrite[1] in its present form is not satisfactory. The results are unreliable.

The potassium perchlorate method, more commonly called the Wense[2]-Caspari[3] method, has been applied to the analysis of fertilizers and similar material containing alkalies, alkaline earths, iron, aluminium, magnesium, and phosphates. The chief difficulty in this method has been the obtaining of the perchloric acid. The danger of preparing the pure acid, as was attempted, is very great. For this reason the method has not been available to many chemists. Recently a 20% solution at $3.00 a Kilo, a 30% solution at $4.80 a Kilo, and even stronger solutions of perchloric acid have been placed on the market.

The quantity of perchloric acid necessary to combine with 1 g. of potassium costs 3.8 cents. The cost of an equivalent amount of chloroplatinic acid is $4.90. The cost of perchloric acid in the perchlorate method is not only lower than the cost of platinum in the chloroplatinate method, but is much lower than the cost of recovering the platinum. The precipitate $KClO_4$, is of constant composition, its solubility in 96% alcohol containing 0.2% $HClO_4$ is almost zero, and the loss by ignition is eliminated. The fertilizer chemists[4] of Germany have tested the method and have obtained such accurate results that they have placed it on an equal basis with the chloroplatinate method by adopting it as an official method.[5]

In this method the sulfates are precipitated in a slightly acid solution. This solution of chlorides is then treated with an excess of perchloric acid, (1.5 times that required to combine with all bases present), and evaporated with constant stirring until white fumes appear. A small amount of water is then added and again evaporated with stirring. This is continued

[1] H. B. McDonnel, Bur. Chem , *Bull* **162**, 19 (1912).

[2] W. Wense, *Z angew Chem* , **4**, 691 (1891), **5**, 233 (1892).

[3] R. Caspari, *Ibid* , **6**, 68 (1893)

[4] *Landw. Ver. Sta* , **59**, 313 (1903), **67**, 145 (1907)

[5] *Fifth Internat. Congr of Appl. Chem* , **1**, 216 (1903); **4**, 940 (1903)

until all volatile acids are absent. The perchloric acid lost by volatilization is replaced from time to time. The precipitate ($KClO_4$) obtained is washed with 95% alcohol immediately before drying.

The author has modified this method as follows: Precipitate the sulfates in a strong hydrochloric acid solution, avoiding a large excess of barium chloride. Evaporate the resulting solution with only a slight excess of perchloric acid without stirring. Dissolve the residue and again evaporate with perchloric acid. Wash the precipitate only with alcohol containing 0.2% perchloric acid before drying.

The revised method as applied to the determination of potassium in water is as follows: Evaporate an aliquot portion of the water to about 150 cc. Acidify with 10 cc. of concentrated hydrochloric acid and heat to boiling. To the boiling solution add drop by drop (avoiding a large excess), a 10% solution of barium chloride until all the sulfates are precipitated. Boil for fifteen minutes and then filter. If no precipitate forms, filtration may be omitted.

Evaporate the filtrate to dryness. Heat until all the ammonium salts are driven off. Dissolve in 20 cc. of hot water and add a quantity of a 20% solution of perchloric acid, slightly in excess of that required to combine with nearly all bases present. One cc. of perchloric acid is equivalent to 90 mg. of potassium (K). Evaporate to dryness. Add 10 cc. of hot water and a small amount of perchloric acid. Again evaporate to dryness. If white fumes do not appear, take up with 10 cc. of water, add more perchloric acid and evaporate to dryness. Repeat until white fumes do appear. Take up with 25 cc. of 96–97% alcohol, containing 0.2% perchloric acid (1 cc. of 20% $HClO_4$ per 100 cc. of 97–98% alcohol). Break up the residue with a stirring rod. Decant the supernatant liquid through a Gooch crucible containing a matt that has been washed with 0.2% perchloric acid in alcohol. If there is an unusually large precipitate, dissolve it in hot water and repeat the evaporation with perchloric acid. (Large quantities of barium chloride are difficult to change to the perchlorate.) Wash once by decantation with 0.2% perchloric acid in alcohol, and transfer the precipitate to the crucible. Wash several times with 0.2% perchloric acid in alcohol. Dry the crucible in an oven at 120–130° for an hour. Remove, cool and weigh. The increase in the weight of the crucible is $KClO_4$. (In using the Gooch crucibles, do not disturb the matt after analysis. Dissolve the potassium perchlorate with hot water, leaving the matt intact. Using the crucible repeatedly in this manner eliminates the errors due to the action of perchloric acid on fresh asbestos.)

If both sodium and potassium are to be determined, obtain the combined chlorides by the usual methods, and estimate the potassium as

potassium perchlorate, as described, omitting the precipitation of the sulfates with barium chloride.

It is of advantage to evaporate to dryness with only a slight excess of perchloric acid, and to repeat the process a second and possibly third time, in order to insure the removal of nearly all volatile acids, and in order to make stirring while evaporating unnecessary.

The recommendation of 97% alcohol for washing is due to the solubility of potassium perchlorate in alcoholic solutions of perchloric acid containing 95% or less alcohol. The difference between the efficiency of 97% and 100% alcohol is immaterial.

It is undesirable to wash the crucible with ether or alcohol just before drying. A slight amount of potassium perchlorate would be dissolved. Dry as much as possible with air suction and then dry in an oven. The small amount of perchloric acid left in the asbestos will be volatilized without causing any error, especially if the same asbestos matt is used repeatedly.

A series of analyses was first made using only potassium chloride. (See Table I.) This potassium chloride, the purest of a well-known firm, was dried at 180° for several hours before using. A standard solution was then prepared and definite amounts measured out with a standardized pipet.

TABLE I —ANALYSES OF SOLUTIONS CONTAINING ONLY POTASSIUM CHLORIDE.

No	Potassium added, g	KClO$_4$ obtained, g	Potassium obtained, g	Error, g
1	0 0050	0 0174	0 0049	—0 0001
2	0 0100	0 0353	0 0100	. . . .
3	0 0150	0 0530	0 0150	. . .
4	0 0200	0 0701	0 0198	—0 0002
5	0 0300	0 1049	0.0296	—0 0004
6	0 0350	0 1241	0 0350	. . .
7	0 0500	0 1769	0 0499	—0.0001

Since the amount of potassium found agreed with the amount taken, a second series was analyzed, using comparatively large amounts of sodium chloride in addition to the potassium. (See Table II.)

The variations are small and lie within the limits of experimental error. The largest is —0.9 mg. The average for the fifteen analyses is 0.2 mg. less than the theoretical amount. The balance used is not capable of weighing less than 0.1 of a mg. The error in percentage, is large with small quantities (amounting to as much as 2.0%). Increasing the quantity of potassium decreases the error in percentage.

An artificial mineralized water was then made by adding the following constituents to distilled water: $CaCO_3$, $MgCO_3$, $MgCl_2$, Na_2CO_3, NaCl and Na_2NO_3. The insoluble constituents were dissolved with a small amount of hydrochloric acid. Portions of this solution containing 0.1

TABLE II.—ANALYSES OF SOLUTIONS CONTAINING LARGE QUANTITIES OF SODIUM CHLORIDE.

No.	Potassium added, g.	Sodium chloride in solution, g.	KClO₄ obtained, g.	Potassium obtained, g.	Error. G	%.
1	0 0050	0 0500	0 0181	0 0051	+0 0001	+2 0
2	0 0100	0 1000	0 0350	0 0099	—0 0001	—1 0
3	0 0200	0 2000	0 0712	0 0201	+0 0001	+0 50
4	0 0300	0 3000	0 1073	0 0302	+0 0002	+0 66
5	0 0400	0 4000	0 1423	0 0401	+0 0001	+0 25
6	0 0500	0 5000	0 1783	0 0503	+0 0003	+0 60
7	0 0600	0 6000	0 2129	0 0600	0 0000	0 00
8	0 0700	0 7000	0 2471	0 0697	—0 0003	—0 40
9	0 0800	0 8000	0 2830	0 0799	—0 0001	—0 11
10	0 1000	0000	0 3534	0 0997	—0 0003	—0 30
11	0 2000	0000	0 7090	0 2001	+0 0001	+0 05
12	0 3000	0000	1 0626	0 2999	—0 0001	—0 03
13	0 4000	0000	1 4171	0 3999	—0 0001	—0 03
14	0 5000	0000	1 7686	0 4991	—0 0009	—0 18
15	1 0000	0000	3 5438	1 0000	0 0000	0 00

g. of each substance (CaCO₃ and MgCO₃ now being present as CaCl₂ and MgCl₂, respectively), were measured out. Known amounts of potassium were then added to each portion and determined without removing any of the ions. The results are shown in Table III   In this series most of the errors, although not large, are minus in character.

TABLE III —ANALYSES OF WATERS OF HIGH MINERAL CONTENT

No	Potassium added, g	Mineral content g	KClO₄ obtained, g	Potassium obtained, g	Error G	%
1	0 0500	0 6000	0 1757	0 0496	—0 0004	—0 80
2	0 1500	0 6000	0 5301	0 1497	—0 0003	—0 20
3	0 2500	0 6000	0 8887	0 2508	+0 0008	+0 32
4	0 3000	0 6000	1 0612	0 2995	—0 0005	—0 17
5	0 3500	0 6000	1 2378	0 3493	—0 0007	—0 20

To each of several portions of the same artificial water 0.1 g. of Na₃PO₄ was added, and the potassium determined as above, with results as shown in Table IV.

TABLE IV —ANALYSES OF HIGHLY MINERALIZED WATER CONTAINING PHOSPHATE

No	Potassium added, g	Mineral content, g	KClO₄ obtained, g	Potassium obtained, g	Error G	%
1	0 0500	0 7000	0 1784	0 0503	+0 0003	+0 60
2	0 1000	0 7000	0 3540	0 0999	—0 0001	—0 10
3	0 1500	0 7000	0 5323	0 1502	+0 0002	+0 13
4	0,2500	0 7000	0 8867	0 2501	+0 0001	+0 04
5	0 3500	0 7000	1 2385	0 3494	—0 0006	—0 17

Though sodium phosphate is insoluble in alcohol, it does not produce an error in the determination of potassium (see Table IV). When sodium phosphate is evaporated with HClO₄ the following reaction takes place.

$$Na_3PO_4 + 3HClO_4 = 3NaClO_4 + H_3PO_4$$

Sodium perchlorate and phosphoric acid are soluble in alcohol and do not cause an error in the determination of potassium.

The sulfate and ammonium ions were found to produce an error, but the error caused by the sulfate was not equivalent to all the sulfate ion that was present.   It is necessary to remove all of the ammonium salts and most of the sulfates.

Summary.

The method of determining potassium as the perchlorate is accurate.

Sulfate and ammonium ions produce an error and must be removed. The sulfate is precipitated with barium chloride in a strongly acid solution avoiding a large excess.   The ammonium salts are expelled by heating.

The phosphate ion does not produce an error and need not be removed.

The solution containing chlorides should be evaporated to dryness with a slight excess of perchloric acid, without stirring.

The precipitate should be washed only with alcohol containing 0.2% perchloric acid.

The time of making an analysis is short, the manipulations are simple, and the cost is almost negligible.

The method can be recommended for use in water analyses and in other analytical work where the content of potassium is desired.

ILLINOIS STATE WATER SURVEY,
UNIVERSITY OF ILLINOIS,
URBANA, ILL.

A NEW METHOD FOR THE PRECISE STANDARDIZATION OF HYDROCHLORIC ACID SOLUTIONS.

BY LAUNCELOT W. ANDREWS.

When the greatest precision is desired in standardizing a volumetric solution, those methods should be avoided, which: (1) involve transferring or washing a precipitate; (2) depend upon the peculiarities of any particular indicator; (3) require the use of standard substances containing water of crystallization, or those that may contain impurities difficult to detect, *i. e.*, almost all organic compounds, or that can not be positively dried without danger of decomposition; (4) demand any peculiarities of technique or any exercise of personal judgment that may make it difficult for different observers to obtain nearly identical results.

With these criteria in mind, I have devised and for several years used in practice a method, the accuracy of which is only limited by the unavoidable errors of weighing.   It depends upon the loss of weight caused by the replacement of NO_3 in silver nitrate by Cl.   Since hydrochloric acid solutions kept in glass vessels, always contain traces of chlorides and of other non-volatile impurities derived from the glass, the process must be so conducted as to avoid error from this source.   The method is carried out as follows, when the solution to be standardized is 0.2 N:

Select two porcelain, or better, silica dishes, of approximately like size, form, and weight, of 75 to 100 cc. capacity, each being provided with a light watch glass or silica cover, and one of them with a silica or glass rod, short enough to lie under the cover. The dish without a rod will be referred to as the "companion dish." In the former, place 1.9 to 2.0 g. of the purest silver nitrate. The absence of ammonium nitrate should be assured. Both dishes are put into an oven at 160°, the temperature raised to 240° and kept there till the weight is constant. At this temperature no water is retained. After cooling in a desiccator, weigh both dishes, covered. Leaving both covers in the balance case, remove the dishes.

By means of a pipet, measure 50 cc. of 0.2 N hydrochloric acid, to be standardized, into the dish with the silver nitrate, using, of course, every precaution to make the measurement as accurate as possible, and noting the temperature of the solution. At the same time, measure 50 cc. of the same acid into the companion dish.

Stir up the silver nitrate until all has dissolved and the silver chloride has clotted together, but do not remove the rod from the dish. Place both dishes in the steam bath at 95–100°, to evaporate the water without spattering, and finally dry at the temperature at which the silver nitrate was dried Cool in the desiccator and weigh. The increase in the weight of the companion dish is assumed to represent the weight of non-volatile impurities contained in the acid, and its amount is subtracted, as a correction, from the observed weight of the silver chloride. This arrangement compensates for changes in the apparent weights due to atmospheric changes, so that, in case of very pure hydrochloric acid, the change of weight in the companion dish may be negative, a circumstance that need cause no apprehension.

By drying the silver nitrate, and, later, nitrate plus chloride, at the temperature of incipient fusion of the former, the same results are obtained as at 200° or 240°.

The normality of the solution is given by the expression:

$$N = \frac{W - W_1 + w_1 - w}{0.02655 \ V}$$

in which,

V = Corrected volume of solution.

W = Weight in air of $AgNO_3$ + dish.

W_1 = Weight in air of AgCl + $AgNO_3$ + dish.

w = Weight of companion dish before.

w_1 = Weight of companion dish after.

In testing experimentally the precision of this standardizing method, it was esteemed better to eliminate errors due to volumetric measurement of the solution, and to weigh the latter instead. Agreement of the re-

sults among one another will show whether any chlorine escapes or whether any other variable sources of error lie in the chemical reaction itself. The results of four such determinations follow. The weight of dish, cover and rod was less than 70 g.

Exp. A   Dish + $AgNO_3$ minus weight after = 0 5311 g $w_1 - w$ = 0 0001. Wt sol 50 0445 g

Exp B   Dish + $AgNO_4$ minus weight after = 0 5316 g $w_1 - w$ = 0 0004 Wt sol 50 0548 g

Exp. C.   Dish + $AgNO_8$ minus weight after = 0 53105 g $u_1 - w$ = 0 0001 Wt sol 50 0391 g

Exp D   Dish + $AgNO_3$ minus weight after = 0 5310 g $w_1 - w$ = 0 00005. Wt sol 50 0396 g

Hence, the loss (corrected by companion dish) is respectively, per 50 g. of solution taken: in A 0.53063, in B 0.53062, in C 0.53095, in D 0.53054. Since the balance was sensitive to only 0.05 mg. it is evident that errors of weighing alone account fully for the surprisingly small variations observed. It is, further, clear that these errors may be diminished if there were any object in so doing, by operating with normal instead of 0.2 N solutions. The disadvantage that the loss of weight is a smaller quantity than the absolute weight of the HCl determined, so that all errors are multiplied by the factor 1.37, is made unimportant by the great accuracy of the process in itself. In spite of its precision, the method is not time-consuming, as the evaporations require no oversight. The time spent is, practically, only that required by the weighings. Most of this work was done in the laboratory of the Andrews Chemical Works, Davenport, Iowa.

WASHINGTON, D C

CORRECTION.

Correction for article on "The Potential of Silver in Nonaqueous Solutions of Silver Nitrate," by Vernette L. Gibbons and F. H. Getman, which appeared in the August number of THIS JOURNAL, page 1645· The last five values in Table X should have been headed Table XI -Solutions in Pyridine.

BENZOYLATIONS IN ETHER SOLUTION.

BY WILLIAM M DEHN AND ALICE A BALL Received July 20, 1914.

In a former paper[1] it was shown that acetyl chloride reacts in anhydrous ether solutions with primary, secondary and tertiary bases. The initial products were invariably additive products and these, by simple splitting or by hydrolysis, yielded the ordinary acetylated products.

[1] THIS JOURNAL, 34, 1399 (1912)

This paper includes analogous studies with benzoyl chloride. With this, as with acetyl chloride, the hydrochlorides of the original base and the acyl chloride additive products of the original bases were precipitated as mixtures. These were often contaminated with the original bases or with benzoylated bases, when such were insoluble in ether; as in cases of the aromatic derivatives benzanilide, benztoluidides, benznaphthalides,[1] benzphenylhydrazine, etc. The courses of these reactions are indicated in the equations:

$$(1) \quad BzCl + 2RNH_2 \longrightarrow RBzNH \cdot HCl \rightleftharpoons HCl + RBzNH$$
$$\searrow RNH_2 \cdot HCl \nearrow$$

$$(2) \quad BzCl + 2R_2NH \longrightarrow R_2BzN \; HCl \rightleftharpoons HCl + R_2BzN$$
$$\searrow R_2NH \cdot HCl \nearrow$$

$$(3) \quad BzCl + R_3N \rightleftharpoons R_3BzNCl$$
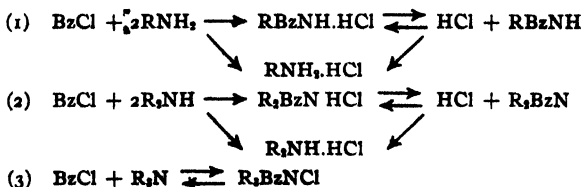
For the purpose of excluding moisture, the benzoyl chloride was redistilled with proper protection from the atmosphere when 60 g. were transferred to two liters of anhydrous ether. The latter was siphoned into a self-filling 100 cc. buret, the flask and buret being supplied with calcium chloride tubes. Glass-stoppered, amber-colored bottles of proper size were previously dried by lumps of fused calcium chloride. Into these, 100 cc. of the ether solution, containing 3 g. of benzoyl chloride, were run, so that the ether solution was at no time in contact with atmospheric moisture. The stopper of each bottle having been sealed with paraffin, the solutions were set aside, to be treated, when desired, with one molecular weight of the anhydrous base. If the base was insoluble in ether, it was powdered and added directly; contact with the latter solutions was promoted by shaking.

When it was found that the amber-colored glass of the bottles retarded the reactions, the contents of the bottles were transferred to colorless, previously desiccated, bottles. In the latter bottles the accelerating influence of sunlight could be observed. It was found that most of the compounds crystallized on the inner surfaces of the bottles facing the direct sunlight. Often the rate of precipitation was retarded when the sides of the containers became coated, but further precipitation could be obtained either when the precipitate was shaken off or when the liquid was transferred to another container.

The precipitates were filtered rapidly, washed with anhydrous ether and dried in desiccators. In some cases the additive products were so hygroscopic that their melting points and analyses could not be obtained without considerable error. In some cases the products were analyzed in the containers in which they were formed; in other cases, as with *p*-

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[1] For the complete analysis of a typical mixture see that of α-naphthylamine.

benztoluidide hydrochloride, indirect methods of analysis were resorted to.

The analyses for halogen were made by the Volhard method. The percentages found were equal to: (1) the percentages of chlorine contained in the hydrochloride of the original base; (2) some percentage lying between this and the percentage of the additive compound; (3) the percentage contained in the additive compound; and (4) some percentage less than the percentage of the additive compound. Thus there were indicated: (1) the hydrochloride of the original base; (2) a mixture of this with the additive compound and sometimes with the benzoylated base, (3) the additive compound; and (4) a mixture of this with a preponderance of the benzoylated base.

The benzoyl chloride additive products of the primary and secondary bases were prepared by two methods: (a) as indicated by reactions (1) and (2); and (b) by adding hydrogen chloride[1] to anhydrous ether or hydrocarbon solutions of the benzoylated derivatives indicated in (5) and (6). The latter method, of course, yielded pure products; the former method, for reasons indicated, yielded mixtures.

With the additive products of benzoyl chloride as of acetyl chloride, spinning motions[2] were produced when the substances were floated on water. Since these motions were produced even by mixtures with low percentages of the additive products, such movements invariably served as a test for their presence.

Many of these pentavalent nitrogen derivatives of the bases are unstable toward heat and all are extremely unstable toward water. For instance, the benzoyl chloride additive product of p-toluidine decomposes in a desiccator at $19°$, in accordance with the reaction:

$$(4) \quad CH_3C_6H_4.BzNH.HCl \longrightarrow CH_3C_6H_4.BzNH + HCl$$

Towards water, the benzoyl chloride additive products of the respective bases react as follows:

$$(5) \quad RBzNH.HCl + H_2O \longrightarrow RBzNH + H_2O.HCl$$

$$(6) \quad R_2BzN.HCl + H_2O \longrightarrow R_2BzN + H_2O.HCl$$

$$(7) \quad R_3BzNCl + H_2O \longrightarrow R_3N + BzOH + HCl$$
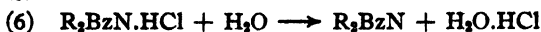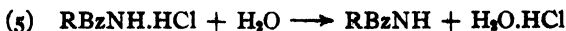
Thus it is observed that heat and water yield the same dissociated products. On account of their instability toward heat and especially toward water, their preparation and handling required correct physical conditions, especially the rigorous exclusion of moisture. The bases were dried with fused potash and usually were distilled over metallic sodium in thoroughly desiccated vessels. However, owing to the small molecular weight of water

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[1] The best method used for adding the hydrogen chloride was by means of a solution of it in toluene. The concentration of this was determined by titration, and thus equimolecular quantities could be added.

[2] THIS JOURNAL, **34**, 1400 (1912).

as compared with that of benzoylated derivatives, even traces of moisture often yielded a preponderance of the secondary products.

The trace of water may react in accordance with Equations 5 and 6 forming hydrochloric acid, which in turn may react with the original base, forming the salt and freeing the water. Thus a trace of moisture may catalytically yield a preponderance of salt of the original base. When the speed of reaction is rapid, benzoyl chloride and the base being present in equimolecular quantities, this influence may not operate so largely. This is seen in cases of piperidine and benzylethylamine; the former, precipitating rapidly, yielded 32% and the latter, precipitating slowly, yielded 18% of the additive compounds.

A condition of supersaturation of the ether solution may also intervene, thus favoring the kinetic dissociation of the additive product, so as to yield a preponderance of salt of the original base. That this influence does not operate in cases of the tertiary bases is owing to the absence of hydrogen chloride.

The formation of additive compounds, when benzoyl chloride acts upon bases in anhydrous ether, cannot be explained on the basis of ionization for the reasons: (1) a non-ionizing medium is used; (2) the speeds of reaction vary widely with different bases; (3) sunlight, which is not recognized as an accelerator of ionization, promotes all of the condensations; and (4) other phenomena not reconcilable with ionization are observed.

Of course, it may be maintained that a trace of water promotes the ionization of benzoyl chloride and the bases and, indeed, that ether itself is an ionizing medium. If either or both of these assumptions are true, the speed of reaction should be equal or nearly equal with different bases, for the reason that, while the degrees of ionization of the bases differ but little, the other factors are constants. However, the various precipitations involved times extending from a few seconds to many weeks, hence other variables are involved in the different reactions. That the delayed precipitations were not the results of supersaturation is evident from consideration of the facts that: (1) the precipitations were continuous over the times involved, and (2) the precipitations were promoted by direct sunlight. It appears, therefore, that the important variables involved in reactions of this kind are: (1) the affinity constants of the different bases, and (2) the factor of sunlight energy.

Without involving use of the ionic theory, it may be assumed that the respective bases, with different affinity constants, manifest different tendencies to coalesce with benzoyl chloride; this tendency has its basis in the residual valencies of the two compounds involved. For instance, the bases acted upon are all trivalent but potentially pentavalent; the benzoyl chloride contains the unsaturated atoms oxygen and chlorine. Therefore, it is possible that the initial reaction is:

(8) $R_3N ==\; +\; == ClCOC_6H_5 \rightleftharpoons R_3N == ClCOC_6H_5$

This coalescence may be assumed to be partial and reversible, the direct progress depending upon the respective affinity constants of the bases The molecular compound formed may represent greater or less tendency to undergo molecular rearrangement, as indicated in the equation

(9) $R_3N == ClCOC_6H_5 \rightleftharpoons R_3(COC_6H_5)NCl$
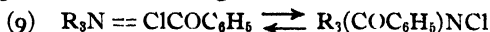
and the promotion of this rearrangement may be caused by the energy of sunlight   Of course, the weakness of this hypothesis is the non-isolation of two isomeric additive products, it would seem that among many different reaction products of this kind, some of the unstable form (8) would be precipitated   Since secondary reactions do not occur with the tertiary bases, only reactions as given in (8) and (9), it is expected that they are best suited for the study of this problem   As a matter of fact, these very bases precipitate two crystalline forms, which at first were assumed to be the benzoyl chloride and the hydrogen chloride additive products, respectively, of the base   Since the hydrogen chloride could not be formed, except by hydrolysis of the benzoyl chloride, the absolute exclusion of water will eliminate the possibility of formation of the hydro chloride   This problem will be taken up anew   In the two following reactions   ·

(10) $RNH_2 + BzCl \longrightarrow RBzNH\; HCl$

(11) $RBzNH + HCl \longrightarrow RBzNH\; HCl$

the end products are the same, hence it may be concluded that the reaction will take place with equal ease   However, this was found not always to be the case   For instance, isoamylamine, aniline, *o*-toluidine and *α*-naphthylamine yielded the additive product with ease, but their respective benzoylated derivatives *failed*[1] *to yield with hydrogen chloride the same additive products*   When it is remembered that hydrogen chloride is more stable toward heat than benzoyl chloride, it may be understood how, in accordance with the coalescent hypothesis

(12) $R\; H_3N\; =\; Cl\; Bz$ ⟍

$R\; BzHN\; =\; Cl\; H \longrightarrow RB_7HN\; HCl$
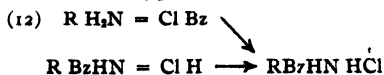
the benzoyl group and the hydrogen atom attached to chlorine may manifest different tendencies to shift to the nitrogen atom and thus to yield the particular additive product   Of course, since the hydrogen chloride in many cases yields the additive product, the affinity of the trivalent nitrogen molecules must exert different influences on the hydrogen atom attached to chlorine.   Thus both these different affinity constants and the

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[1] Equimolecular quantities of benzamide and hydrogen chloride in toluene yielded benzamide hydrochloride   Cf Dessaignes *Ann* **82**, 234 (1852)   Pinner and Klein, *Ber* **10**, 1897 (1877), **11**, 10 (1878)   Meyer *J prakt Chem* [2] **30**, 122 (1843)

tendency of (H) and (Bz) to dissociate from (Cl) are probably factors of the chemical changes.

Primary Bases.

Isobutylamine.—When equimolecular quantities of isobutylamine and benzoylchloride were brought together in anhydrous ether, an immediate heavy precipitate was formed. It contained 28.07% Cl.

Calculated for $C_4H_9NH_2.HCl$: Cl, 29.66%; for $C_4H_9.C_6H_5CONH.HCl$: Cl, 16.60%.

From these data it was calculated that *isobutyl benzamide hydrochloride* was present as 11.71% of the mixture. Its presence was further indicated by the spinning motions produced when the mixture was floated on water. After being washed with water, dried and concentrated, the ether solution yielded large transparent rectangular plates of isobutylbenzamide[1] melting at 58° and boiling at 305–308°. Anhydrous ether and xylene solutions yielded some oil but no crystalline isobutylbenzamide hydrochloride.

Isoamylamine.—When equimolecular quantities of isoamylamine and benzoyl chloride were brought together in anhydrous ether, pearly flakes, softening at 160°, melting at 201° and containing 16.09% of chlorine, were obtained.

Calculated for $C_5H_{11}.C_6H_5CONH.HCl$: Cl, 15.56%. Calculated for $C_5H_{11}NH_2.HCl$: Cl, 28.69%.

Since both isoamylamine and isoamylbenzamide[2] are soluble in ether, the precipitate contained only *isoamylbenzamide hydrochloride.* Its presence was further indicated by spinning and darting motions produced when the substance was floated on water. The ether solution and some of the precipitate were treated with dilute alkali; the ether solution was separated, dried and concentrated. An oil boiling at 310–315° was obtained; evidently it was *isoamylbenzamide,* $C_5H_{11}.C_6H_5CONH$ with hydrogen chloride in anhydrous ether toluene xylene yielded a liquid hydrochloride.

Aniline.—An immediate precipitate was formed. It was incompletely soluble in water and contained 10.18% of chlorine.

Calculated for $C_6H_5.C_6H_5CONH.HCl$: Cl, 15.18%. Calculated for $C_6H_5NH_2.HCl$: Cl, 27.39%.

Since the percentage of chlorine was lower than either of these, it contained benzanilide.[3] This was obtained by adding water to some of the precipitate—leaflets melting at 161° were obtained. That the original precipitate contained *benzanilide hydrochloride* was further indicated by spinning

[1] Wheeler, *Am. Chem. J.,* **23,** 142; Titherley, *J. Chem. Soc.,* **79,** 406.

[2] Wurtz, *Ann.,* **75,** 334; THIS JOURNAL, **34,** 1404 (1912).

[3] Wallach and Hoffman, *Ann.,* **184,** 80; Gerhardt, *Ibid.,* **60,** 311; Lossen, *Ibid.,* **175,** 310; Leuckart, *J. prakt. Chem.,* [2] **41,** 306; Beckman, *Ber.,* **20,** 1508, 2581; Nageli, *Bull. soc. chim.,* [3] **11,** 893; Schweder, *Ber.,* **12,** 1613; Berthelot, Fogh, *Ibid.,* **12,** 1613; Cohen, *J. Chem. Soc.,* **59,** 71; Meyer and Sundmacher, *Ber.,* **32,** 2123; Dinglinger, *Ann.,* **311,** 153.

motions when it was floated on water.   It could.not be prepared by adding hydrogen chloride to a toluene solution of pure benzanilide.

p-Toluidine.—An immediate, voluminous precipitate was formed   It was incompletely soluble in water and contained 9.35% of chlorine.

Calc. for $CH_3C_6H_4.C_6H_5CONH.HCl$: Cl, 14.32%. Calc. for $C_7H_7HN_2.HCl$: Cl, 24.70%.

The insoluble portion was identified as *p*-tolylbenzamide, melting at 158°. That the original precipitate contained *p-tolylbenzamide hydrochloride* was indicated by the spinning motions.   It was prepared in pure form by passing hydrogen chloride into a xylene solution of *p*-tolylbenzamide. When isolated it was found to be decomposed even in a desiccator at ordinary temperatures into *p*-tolylbenzamide[1] and hydrogen chloride.   That the crystals were the additive compound was proven by the following method of analysis: After the crystals were formed in the manner indicated above, the apparatus was aspirated with dry air to remove the excess of hydrogen chloride.   Without exposing the contents of the vessel to atmospheric moisture, the xylene was siphoned off and the crystals were washed with more dry xylene, which was also siphoned off.   More xylene was added and also some distilled water.   The crystalline compound being hydrolyzed, the hydrogen chloride dissolved in the water and the *p*-tolylbenzamide dissolved in the xylene.   The former was estimated by titration with silver nitrate; the latter, by evaporating the xylene solution.   From these data it was calculated that the crystals contained 14.80% of chlorine.

Calc. for $C_7H_7.C_6H_5CONH.HCl$: Cl, 14.32%.

Equimolecular quantities of *p*-tolylbenzamide and hydrogen chloride in toluene did not yield any precipitate of the hydrochloride.

o-Toluidine.—An immediate precipitate containing 10.47% of chlorine was obtained.   Since spinning motions were obtained with water and the insoluble portion melted at 142°, the precipitate evidently was a mixture of *o*-toluidine hydrochloride, *o*-tolylbenzamide[2] and *o-tolylbenzamide hydrochloride*.   The last mentioned could not be prepared by passing hydrogen chloride into a xylene solution of *o*-tolylbenzamide.

m-Toluidine.—An immediate precipitate, showing spinning motions on water and containing 11.00% of chlorine, was obtained.   That it was a mixture of *m*-toluidine hydrochloride, *m*-tolylbenzamide[3] and *m-tolylbenzamidehydrochloride* is sufficiently evident.

α-Naphthylamine.—When 3 g. of benzoyl chloride and 3.06 g. of α-

[1] Jaillard, *Z. Chem.*, 1865, 400; Hübner, *Ann.*, 208, 310; Wallach, *Ibid.*, 214, 217; Apitzsch, *Ber.*, 33, 3524.

[2] Büchner, *Ann.*, 205, 130, gives melting point at 142-143°; Güdeman, *Ber.*, 21, 2553, gives melting point at 131°.

[3] Just, 19, 983, gives m. p 125°.

naphthylamine were brought together in anhydrous ether, an immediate voluminous precipitate was formed. It was filtered and the ether solution gave, by evaporation, 2.53 g. of a mixture of α-naphthylbenzamide and unchanged benzoyl chloride. The precipitate weighed 3.504 g. and contained 7.84% of chlorine

Calc for $C_{10}H_7NH_2$ HCl   Cl, 19 74%   Calc for $C_{10}H_7$ C_6H_5CONH HCl Cl, 12 50%

Upon adding water to the precipitate, spinning motions indicated the presence of the additive compound. The insoluble portion, consisting of α-naphthylbenzamide[1] and melting at 156°, weighed 1 942 g., the aqueous solution yielded by evaporation (a) 1.4577 g of α-naphthylamine hydrochloride   The difference between the sum of these weights and the weight of the original precipitate was 0.1043 g or the hydrogen chloride united with α-naphthylbenzamide in the additive compound, and rendered free by the action of water on the original precipitate   Since this hydrogen chloride is equivalent to (b) 0.8111 g. of *α-naphthylbenzamide hydrochloride*, the original mixture consisted of·

		Grams	Per cent
(a)	$C_{10}H_7NH_2$ HCl .	1 4577	41 60
(b)	$C_{10}H_7$ C_6H_5CONH HCl	0 8111	23 15
(c)	$C_{10}H_7$ C_6H_5CONH .	1 2352	35 25

Making use of the fact that the aqueous portion (1 562 g) contained 18.30% of chlorine, it may be calculated that 28.45% of the original precipitate was an additive compound. From these two analyses it is concluded that the original precipitate contained 23-28% of *α-naphthylbenzamide hydrochloride*. This compound could not be formed by passing hydrogen chloride into solutions of α-naphthylbenzamide in alcohol-ether, benzene or xylene.

Phenylhydrazine.—An immediate, voluminous precipitate, containing only 3.17% of chlorine was obtained.

Calc for $C_6H_5N_2H_3$ C_6H_5COCl Cl, 14 27%   Calc for $C_6H_5N_2H_3$ HCl Cl, 24 53'¿

With water, the precipitate showed darting motions and yielded insoluble benzoylphenylhydrazine melting at 166°. The precipitate was a mixture of phenylhydrazine hydrochloride, benzoylphenylhydrazine,[2] and *benzoylphenylhydrazine hydrochloride*. The last was prepared by passing hydrogen chloride into xylene containing benzoylphenylhydrazine   When washed by decantation with anhydrous ether and preserved in a desiccator, fumes of hydrogen chloride and a residue containing little chlorine were

[1] Ebell, *Ann* , **208**, 324, gives m p 165°, Kühn, *Ber* , **18**, 1477, gives m p 161-162°, Hofmann, *Ibid* , **20**, 1798, gives m p. 159-160°; Worms, *Ibid* , **15**, 1814

[2] The melting point is given at 168°   Fisher, *Ann* , **190**, 125, Just, *Ber* , **19**, 1203, Bamberger, *Ibid* , **27**, 162, Holleman and Antusch, *Rec trav chim* , **13**, 9423; Bhidakowski and Slepak, *J Russ Phys Chem* , **35**, 68

obtained. Evidently the compound is dissociated at ordinary temperatures

Acetamide —Though the solution was kept in the sunlight for most of five months, only a little amorphous precipitate,[1] containing 22 96% of chlorine was obtained

Calc for $CH_3CONH \cdot HCl$ Cl 37 12% Calc for $C_6H_5CO(CH_3CO)NH$ HCl Cl 17 77%

Urea —The solution very slowly precipitated clusters of transparent, thick, hexagonal plates clinging to the sides of the bottle, and containing 17 91% of chlorine

Calc for $CON H_4 C_6H$ COCl Cl 17 68%

Ureabenzoylchloride melts at 209° with decomposition and dissolves in water with slow motions

Glycocoll —After ten weeks, amorphous glycocoll, insoluble in ether, was partially replaced by clusters of transparent, prismatic needles, containing 5 76% of chlorine

Calc for $C_2H_3O_2NH_2$ HCl Cl 32 06% Calc for C_6H_5CO C_2H_3O NH HCl Cl, 6 45%

Since no spinning motions were observed, and no benzoic acid could be recovered from the aqueous solution, it is concluded that t e crystals were glycocoll hydrochloride[2] mixed with unchanged glycocoll

Secondary Bases.

Diethylamine – An immediate precipitate containing 29 19% of chlorine was obtained

Calc for $(C_2H_5)_2NH$ HCl[3] Cl 32 36% Calc for $(C_2H_5)_2C_6H_5CON$ HCl Cl 16 60%

Since diethylamine[4] is soluble in ether, the percentage of chlorine indicated that the mixture contained 20 14% of *diethylbenzamide hydrochloride*, the presence of this was confirmed by the spinning motions of the mixture on water

Methylaniline —Crystals forming quite slowly clinging to the side of the bottle and containing 23 03% of chlorine were obtained

Calc for $C_6H_5 CH_3 C_6H_5CON$ HCl Cl 14 32% Calc for $C_6H_5 CH_3 NH$ HCl Cl 24 70%

If phenylmethylbenzamide[5] was not contained in the mixture, 16 09% was *phenylmethylbenzamide hydrochloride*

[1] THIS JOURNAL **34**, 1403 (1912)

[2] Curtius and Gobel, *J prakt Chem* [2] **37**, 157 Schabus *Jahrsb*, **1854**, 676, Kraut and Hartmann, *Ann*, **133**, 100

[3] Wallach, *Ann*, **214**, 275, Behrend *Ibid*, **222**, 119 Pinner *Ber* **16**, 1650

[4] Since diethylbenzamide is a liquid boiling at 280–282° and is soluble in ether it was not a component of the mixture Hallman prepared it in the above indicated manner, *Ber*, **9**, 846 Ramburgh, *Rec trav chim*, **4**, 387

[5] Hepp gives m p 59° *Ber* **10**, 329, Hess gives m p 63°, *Ibid* **18**, 685, Wislicenus and Goldschmidt, *Ibid*, **33**, 1471

Piperidine.—An immediate, very hygroscopic precipitate, containing 24.70% of chlorine, was obtained.

Calc. for C₅H₁₁N.HCl: Cl, 29.17%.   Calc. for C₅H₁₀N.C₆H₅CO.HCl: Cl, 15.72%.

If not containing benzoylpiperidine,[1] the mixture was composed of 33% of *benzoylpiperidine hydrochloride.* This was prepared by treating the former with hydrogen chloride in anhydrous ether solution. First crystals, then an oil, on standing, white, hygroscopic needles containing 16.50% of chlorine were obtained, hence nearly pure additive compound was obtained.

Benzylethylamine.—A slow-forming precipitate containing 19.30% of chlorine was obtained.

Calc. for C₆H₅CH₂ C₂H₅NH.HCl: Cl, 20 66%.   Calc. for C₆H₅CH₂ C₂H₅.- C₆H₅CON.HCl: Cl, 12.87%.

The presence of *benzylethylbenzamide hydrochloride* (17.47%) was indicated by the spinning motions of the mixture on water. *Benzylethylbenzamide*, boiling at 218° at 29 mm., was prepared.

Tertiary Bases.

Triethylamine.—Equimolecular quantities of benzoyl chloride and triethylamine gave an immediate precipitate which was increased on standing. The crystals softened at 180°, melted at 238–240° and contained 15.15% of chlorine.

Calc for (C₂H₅)₃N.HCl Cl, 25 77%.   Calc for (C₂H₅)₃NC₆H₅COCl: Cl, 14 67%.

Evidently the substance was a mixture of triethylamine hydrochloride[2] with *triethylaminebenzoylchloride.*

Triamylamine.—The reaction mixture remained in an amber-colored bottle for three weeks without yielding a precipitate. After standing for five weeks more in a clear-glass bottle, a mass of long needles, melting at 117° and containing 9.55% of chlorine was obtained.

Calc. for (C₅H₁₁)₃N.C₆H₅COCl: Cl, 9.64%.

These were nearly pure[3] crystals of *triamylaminebenzoylchloride.* Upon water they gave the characteristic spinning and darting motions.

Dimethylaniline.—In sunlight, transparent, prismatic crystals were gradually formed on the sides of the bottle. They were very hygroscopic and contained 12.90% of chlorine

Calc for (CH₃)₂C₆H₅N.HCl: Cl, 22 50%.   Calc. for (CH₃)₂C₆H₅N.C₆H₅COCl. Cl, 13 55%.

[1] Schotten, *Ber.*, **17**, 2455; **21**, 2238, gives m. p. 48°; Cahours, *Ann. chim. phys.*, [3] **38**, 76

[2] Schiff and Monsacchi, *Z. phys. Chem.*, **24**, 516.

[3] "Triisoamylamine Hydrochloride," Hofmann, *Ann.*, **79**, 22; Malbot, *Ann. chim. phys.*, [6] **13**, 504.

These crystals were nearly pure[1] *dimethylaniline benzoylchloride*.

Diethylaniline.—Crystals melting[2] at 115–120° and containing 14.20% of chlorine were obtained.

Calc for $C_2H_5(C_2H_5)_2N$ HCl Cl, 19 10   Calc for $C_6H_5(C_2H_5)_2N$ C_6H_5COCl Cl, 12 24%

Diethylaniline benzoylchloride was present as 71% of the mixture.

Antipyrine.—Clusters of transparent needles melting at 138° to a blood-red liquid were obtained. The substance contained 11.08% of chlorine.

Calc for $C_{11}H_{12}N_2O$ C_6H_5COCl Cl, 10 47%

Antipyrine benzoylchloride is very soluble in water.

Quinoline.—Precipitated slowly, reddish crystals melting at 112–116° and containing 16.10% of chlorine.

Calc for C_9H_7N HCl Cl, 21 42   Calc. for C_9H_7N C_6H_5COCl. Cl, 13 15%

Evidently *quinoline benzoylchloride* was present as 65% of the mixture.

Pyridine.—A slow-forming precipitate containing 26.30% of chlorine was obtained.

Calc for C_5H_5N HCl Cl, 30 69   Calc for C_5H_5N C_6H_5COCl Cl, 16 15%

Pyridine benzoyl chloride was present as 31% of the mixture.

α-Picoline.—Star-like clusters of needles containing 17.60% of chlorine were obtained.

Calc for C_5H_4N CH_3 HCl Cl, 27 37%   Calc for $C_5H_4N(CH_3)$ C_6H_5COCl Cl, 15 18%

Picoline benzoyl chloride was present as 80% of the mixture.

SEATTLE, WASH

THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE.[3]

[SECOND PAPER.]

By L. H. CONE

Received July 20, 1914

In a previous paper[4] some experiments were described which indicate a very close analogy between the acridyl salts, *e. g.*, salts of diphenyl acridol (I), and the salts of triphenylcarbinol and its analogues (II). The analogy lay in the character of the reaction of the respective halides with metals. Triphenylmethyl chloride and its analogues in solution react with silver and other metals to form highly unsaturated free radicals of the type of triphenylmethyl. These free radicals absorb oxygen from the air to form

[1] Dimethylaniline hydrochloride melts at 83–85°, Scholl and Escales, *Ber.*, **30**, 3134; Menschutkin, *J. Russ. Phys. Chem. Ges.*, **30**, 252; Perkins, *J. Chem. Soc.*, **69**, 1235; Bredig, *Ber.*, **30**, 673

[2] Diethyl aniline hydrochloride melts at 145°, Reynolds, *J. Chem. Soc.* **61**, 457, THIS JOURNAL, **34**, 1408 (1912)

[3] Presented at the spring meeting of the American Chemical Society, Cincinnati April, 1914

[4] THIS JOURNAL, **34**, 1695 (1912)

peroxides. It was shown that diphenylacridyl chloride and also phenyl-
N-methylacridyl chloride, when shaken in nitrobenzene solution with
molecular silver, give highly colored solutions which absorb oxygen. It
was assumed that in these colored solutions free acridyl radicals were
present. A quantitative study was made of these reactions and it was
found that first silver, and then oxygen enter into the reactions in the
proportions given in the following equations:

(a) $C_{25}H_{18}NCl + Ag = (C_{25}H_{18}N) — + AgCl$

(b) $2(C_{25}H_{18}N) — + O_2 = (C_{25}H_{18}N) — O — O — (C_{25}H_{18}N)$
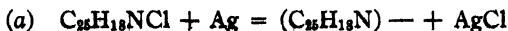
Neither the unsaturated diphenylacridyl, supposed to be formed in re-
action a, nor its peroxide, supposed to be formed in reaction b, were at
that time isolated, but the evidence seemed conclusive that both of these
compounds were produced. This close analogy between the acridyl
chlorides and the triarylmethyl chlorides in so important a reaction as
the formation of free radicals seemed to warrant assigning to the colored
acridyl chlorides the same type of quinocarbonium structure (IV) as that
employed for the colored modifications of the more simple triarylmethyl
chlorides (III).
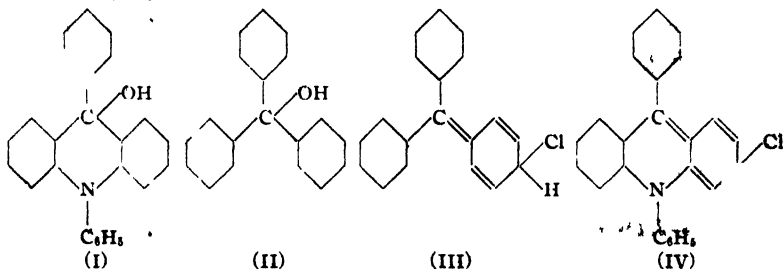
It has now been shown that the interpretation of the reaction between
acridyl chlorides and metals, and then with oxygen as given in equations
(a) and (b), above, is entirely correct. This has been done by actually
isolating several unsaturated radicals and their peroxides. The free rad-
icals as obtained are dark brownish red, beautifully crystalline compounds,
which in solution absorb oxygen from the atmosphere rapidly to form color-
less peroxides. They will also combine directly with halogens to form the
corresponding halide salts. The method which has been found most
satisfactory for the preparation of these free radicals is to shake a watery
solution of some salt, preferably the sulfate, with zinc dust. The zinc
immediately becomes covered with a dark red coating of the free radical,
and if enough zinc has been added the highly colored sulfate solution
is completely decolorized. The colorless watery solution of zinc sulfate
can then be decanted from the zinc and free radical. On addition of benz-
ene to the moist slime the free radical is dissolved, forming a dark red

solution and the excess of zinc appears again in its normal color. The dark red benzene solution is very sensitive to oxidation. If it is shaken a moment in contact with air all of the dark red color disappears and there remains only a pale yellow or brown coloration. From this decolorized solution colorless peroxide soon begins to separate out. In some cases the peroxide is soluble enough in benzene so that it can be recovered only by evaporation of the solvent.

The feature which distinguishes the preparation of free acridyl radicals from the preparation of other triarylmethyls is the use of watery solutions of the acridyl salts instead of benzene solutions as in the other cases. This difference is rendered necessary by the complete insolubility of most acridyl salts in inert organic solvents, and by the non-solubility of the ordinary triarylmethyl chlorides in water. It seems hardly possible that these two classes of salts could all react so completely alike in such a characteristic reaction and yet belong, as is generally supposed, to distinctly different types of compounds, that is, to the quinocarbonium type for the colored forms of the triarylmethyl salts (III) and to the ammonium type for the acridyl salts (V).

(V)
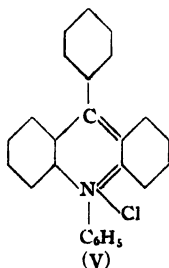
In the absence of any direct experimental evidence that the acridyl salts are really of the ammonium type it seems simpler to assume that they are quinocarbonium in structure (IV) and that the formation of the free radicals consists simply in the removal of the acid radical by a metal. The intensely colored acridyl radicals are certainly analogues of triphenylmethyl. But triphenylmethyl, in solution at least, is not one single substance but is a mixture of substances in equilibrium with each other probably as expressed in the following equation:[1]
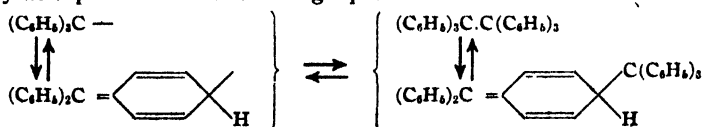
The right-hand side of this equation is the predominant one in the case

[1] Gomberg, THIS JOURNAL, 36, 1167 (1914); Schmidlin, "Das Triphenylmethyl," p. 213.

of triphenylmethyl. The reverse is true for the acridyl radicals, the left-hand or monomolecular side being present in their solutions almost to the exclusion of the other. Of the two monomolecular forms, the upper benzoid, colorless form and the lower quinoid, colored form, the quinoid is probably the predominant one because of the intense color of the radicals and their solutions.

Experimental.

Diphenylacridol (I).—This compound has been prepared by Ullmann[1] and his method has in the main been followed. A few modifications of his method have increased the certainty of good results in carrying out the preparation according to Ullmann. Commercial anthranilic acid is converted by the method of Goldberg into diphenylanthranilic acid and this is then changed to N-phenylacridon by means of sulfuric acid. The N-phenylacridon is converted into diphenylacridol by means of phenyl magnesium bromide. This reaction is described in detail because Ullmann's procedure is varied considerably. The powdered acridon is added in small portions to a 10% excess of phenylmagnesium bromide dissolved in rather a large quantity of ether (one-twentieth mol in about 150 cc.). After a considerable portion of the acridon has been added, an oil begins to separate from the ethereal solution. Without making any further additions of acridon, the ether is now boiled till the oil turns to a yellow solid which can easily be powdered by means of a glass rod. The rest of the acridon is then gradually added, with boiling and shaking after each addition. After all of the acridon has been added the reaction mixture is boiled about two hours. The yellow powder in the bottom of the flask is frequently stirred in order to give the very insoluble acridon every opportunity to enter into reaction. The ether is distilled off, ice and hydrochloric acid are added to the residue and the resulting mixture is steam-distilled to remove benzene and bromobenzene. All but a small portion of the residue will dissolve in dilute acid. To the filtered, cold acid solution, which contains diphenylacridyl chloride, sodium hydroxide is then added till the liquid is decidedly alkaline. Diphenyl acridol and magnesium hydroxide separate out together. The precipitate is filtered, washed a little with approximately normal sodium hydroxide solution and dried in a steam or electric oven to avoid acid fumes. Although the acridol could be precipitated free from magnesium hydroxide by means of ammonium hydroxide, the use of this reagent is not advisable, for then an amino derivative is formed from which it is difficult to free the acridol.[2] The sodium hydroxide is left in the cake of precipitate to keep the acridol from taking up acid from the air during drying. The dried cake is broken up and extracted in a Landsiedl extractor with benzene The benzene

[1] *Ber* , **40,** 2520 (1907)
[2] Villiger, *Ibid* , **45,** 2910 (1912)

solution is concentrated and the acridol thrown out of solution by the addition of petroleum ether.   It can thus be obtained in pure white, crystalline leaflets which melt, as Ullmann gives, at 178°   The yield is 85 to 90% of the theory as calculated from the acridon

Diphenylacridyl Chloride (IV).—A method of preparation of diphenylacridyl chloride has been already described,[1] but a simpler method of obtaining it has now been found.   From a solution of the acridol in chloroform the chloride hydrochloride, $C_{25}H_{18}NCl.HCl$, is prepared by means of acetyl chloride and hydrochloric acid gas as directed in the previous paper   The yellow crystalline chloride hydrochloride is filtered out, redissolved in chloroform and an excess of pure, dry calcium carbonate is added.   The mixture is shaken for some minutes.   The molecule of hydrochloric acid in the hydrochloride is quickly removed to form calcium chloride and acridyl chloride remains in solution.   On concentration of the chloroform solution and gradual addition of petroleum ether, the chloride crystallizes out perfectly pure as glittering yellow plates.

Diphenylacridyl,
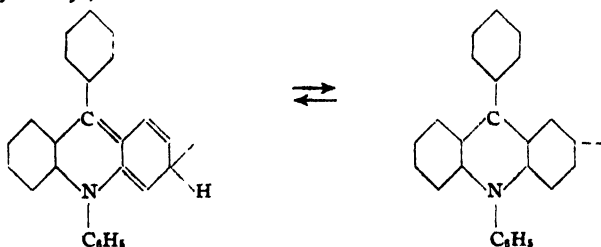
The action of various metals upon diphenylacridyl chloride dissolved or suspended in different solvents has been tried repeatedly.   The metals which were most frequently tested were silver and mercury.   Every attempt to bring about a reaction between these metals and watery solutions of the chloride failed.   It was then found, as reported in the last paper, that the chloride dissolved in nitrobenzene reacts with silver, and that by long shaking the reaction can be brought to completion according to Equation *a* on page 2102   Finally it was found that warm, watery solutions of diphenylacridyl chloride are rapidly decolorized by zinc dust and that the product formed is not colorless diphenylacridane as might be expected but is a brownish red unsaturated compound, diphenylacridyl. Granulated zinc reacts slightly but the surface becomes rapidly coated over with a thin copper-like film of the free radical and further progress of the reaction ceases   Zinc dust seems to be an ideal reagent because of its very large surface   Even this large surface becomes quickly coated over by the free radical which is completely insoluble in water, and the

[1] THIS JOURNAL, **34**, 1699 (1912)

reaction stops unless a great excess of zinc dust (thirty to forty times the theoretical amount) has been used　If a fairly concentrated solution of the chloride is used, its reaction with zinc dust will go rapidly to completion only in hot water. In cold water the reaction starts but the zinc chloride formed unites with still unchanged acridyl chloride to form a rather insoluble double salt and this decreases the rate of the reaction. When the sulfate is used in place of the chloride no double salt is formed and so the reaction is very rapid.

Qualitatively, the reaction can be carried out in a test tube in the most simple manner. In fact, as a lecture room experiment to demonstrate the existence of free radicals and their properties the preparation of diphenylacridyl leaves nothing to be desired in the way of simplicity and certainty. About 1 g. of diphenylacridol is suspended in 25 cc. of water and approximately twice the amount of sulfuric acid necessary to make the normal sulfate is added. The suspension of the acridol is warmed on the steam bath with stirring till the solid has largely dissolved. To the filtered, clear yellow solution sodium hydroxide solution is cautiously added, drop by drop, till a small permanent precipitate of acridol is formed. To this normal sulfate solution 10 g. of zinc dust are added and the mixture is shaken vigorously. The reaction is complete in a fraction of a minute. The dark red slime of zinc dust and free radical settles quickly and the perfectly colorless watery layer can be poured off. The free radical does not oxidize rapidly while in the solid state and wet with water so no special precautions are necessary up to this point to prevent oxidation. The test tube containing the slime is now filled completely with benzene, closed tightly with the thumb and inverted several times. The dark red benzene solution of the free radical is then poured slowly out into a beaker. The solution decolorizes immediately to a pale yellow or brown. After fifteen or twenty minutes' standing in the open the decolorized solution becomes turbid from the separation of peroxide. Thorough decolorization of the benzene solution will take place only if pure diphenylacridol was used in the experiment.

To isolate the solid crystalline diphenylacridyl considerable care is ˙ necessary. The apparatus which has given best results in isolating the compound is the one which has been used in this laboratory for the preparation of solid triphenylmethyl. This has been illustrated and described in detail in *Berichte der deutschen chemischen Gesellschaft*, **37**, 2034. Two similar pieces of this apparatus as described there are necessary. A watery solution of the sulfate, 4 to 5 g. prepared as already described above, is poured into one apparatus. The air is displaced by carbon dioxide, and zinc dust, 15 to˙20 g. slimed up with water, is added to the acridyl sulfate solution. The reaction is quickly completed by shaking. The colorless watery layer is forced out of the apparatus by means of carbon dioxide.

Warm benzene is poured in and the free radical dissolved. The colored benzene solution is decanted from the wet zinc slime over into the second apparatus, passing at the same time through a filter cartridge filled with calcium chloride but without exposing the solution to the air   The benzene solution is then concentrated under reduced pressure till crystallization begins. A volume of petroleum ether, about equal to the benzene solution remaining, is added, the apparatus is filled with carbon dioxide and put in a cool place. Crystallization is complete in relatively short time. The mother liquor is decanted off from the crystals and they are washed with low boiling petroleum ether and dried under reduced pressure. About 2 g. of the crystalline product can thus be obtained from 4 g. of the acridol.

The melting point of diphenylacridyl is *unsharp*, about 185–190°, softening below that temperature   For combustions and molecular weight determinations the diphenylacridyl was dried in a partial vacuum at 80 90° in a slow stream of carbon dioxide. It was necessary to mix the substance with a large quantity of copper oxide in the combustion tube in order to get good results as otherwise it was almost impossible to avoid too rapid decomposition.

Calc for $C_{25}H_{18}N$ C, 90 32, H, 5 46, found   C, 90 17, H, 5 65

Molecular weight determinations were made by the boiling point method in both benzene and chloroform solutions.

		s grams	S grams	d	Mol wt
Benzene	I	0 271	7 45	0 28°	347
	II	0 201	7 45	0 19°	375
Chloroform	I	0 277	22 08	0 13°	348
	II	0 494	22 08	0 23°	350
Calculated for $C_{25}H_{18}N$ = 332					

These determinations show conclusively that under the conditions of the experiments above diphenylacridyl is, largely at least, in the monomolecular state. The results are all slightly higher than the calculated value (332), so there may be some indication of slight association, but boiling point determinations are not accurate enough to warrant any quantitative statement as to the amount of this association.

Diphenylacridyl dissolved in benzene unites instantly with chlorine to form yellow diphenylacridyl chloride. It also dissolves slowly in hydrochloric acid to form the chloride.

Preparation of Diphenylacridyl by Electrolysis of its Salts.—The free radical can be prepared readily by electrolysis. In this method of preparation it is best to use a solution of the neutral sulfate in the absence of all other salts. Finely powdered diphenylacridol is warmed and stirred several hours with less than the necessary amount of sulfuric acid to dissolve it all. The excess of diphenylacridol is filtered off. The sulfate solution is electrolyzed in a wide test tube with a platinum wire sealed

through the bottom. Mercury, to serve as cathode, is added till the platinum wire is covered. The anode is a piece of platinum foil which is suspended in a tube of about 1 cm. diameter. To prevent free mixing of the anode and cathode liquid, the bottom of the anode tube is covered with a double layer of filter paper. The anode tube is set into the large test tube so that the filter paper comes above the mercury. Solid diphenylacridol is added to the liquid in the anode tube for the purpose of combining with acid which is produced there during the electrolysis. The test tube can readily be kept filled with carbon dioxide. 8–10 volts is sufficient for electrolysis. On closing the circuit the ammeter will jump to perhaps half an ampere, and then immediately fall back to practically zero. At the same time a copper-like film of diphenylacridyl appears over the surface of the mercury. By agitating the surface of the mercury the diphenylacridyl breaks away from the mercury in thin scales that float upward in the liquid. The current passing through the solution varies according to the extent of the mercury surface which is free from diphenylacridyl at any time. On account of the high molecular weight of the free radical, its quantity increases rapidly even though the average current is small. As thus prepared the product appears to be beautifully crystalline, but its appearance is deceptive. It is a mass of fine, irregular scales not unlike shellac. By means of suitable apparatus the diphenylacridyl can be separated from the watery sulfate solution and recrystallized from benzene and petroleum ether in the absence of air. This method of preparation is not so satisfactory as the one in which zinc dust is used.

Both the zinc dust method and the electrolytic method of preparation of diphenylacridyl serve to emphasize the metal-like character of the free radical. The salts of diphenylacridyl in watery solution are highly ionized like the salts of sodium or potassium. The precipitation of the free radical from such a solution by means of zinc dust or electrolysis is exactly like the precipitation of copper from its salts by the same methods. In thin films the free radical appears lustrous very like a metal. Like the metals, it dissolves in acids to form salts which are water-soluble. The property of electrical conductivity so characteristic of metals is, however, apparently not possessed by diphenylacridyl in the solid state.

Many attempts have been made in the past to isolate metal like free radicals. The nearest approach to success in this direction has come in the cases of ammonium, methylammonium and tetramethylammonium amalgams.[1] A comparison of the properties of these amalgams with those of diphenylacridyl shows no such resemblances as exist between the latter compound and the triarylmethyls, so there can be no hesitation in classifying diphenylacridyl as other than an ammonium radical. The fact, however, that such a radical as diphenylacridyl with so many metallic

[1] McCoy and Moore, This Journal, 33, 277 (1911).

properties has been prepared, gives reason to believe that free ammonium radicals may yet be isolated and that some of them may be found to be relatively stable compounds.

Diphenylacridylperoxide.—This peroxide is obtained in good yield by exposing a benzene solution of diphenylacridyl to the air and then allowing nearly all of the benzene to evaporate at room temperature. Ether is added to the small residue of benzene, the peroxide is filtered out and washed with more ether. To further purify the still pink peroxide it is recrystallized from carbon disulfide. This is best done by extracting the fine powder in a Landsiedl extractor. It is exceedingly difficult to recrystallize the peroxide in the ordinary manner, *i. e.*, by heating a suspension of the solid and then filtering off the undissolved portion, because so very little goes into solution. In the extraction apparatus, however, as much as 1 g. can be dissolved in 100 cc of boiling carbon disulfide if the extraction is continued two or three hours. On cooling the hot solution from the extractor the peroxide crystallizes out in fine prisms. This crystalline peroxide is pale yellow. It begins to darken at about 190° and melts between 204° and 207° according to the rate of heating. With a moderate rate of heating it will generally melt at 204°.

Calc for $C_{40}H_{24}N_2O_2$ C, 86 17; H, 5 22; found 86 16, 85 60 and 5 16, 5 11

On treating the peroxide with mineral acids it goes slowly into solution to form the corresponding acridyl salts.

Diphenylacridane.—It might be expected when a watery solution of diphenylacridyl chloride is treated with zinc dust that in addition to the free radical some diphenylacridane would be formed.

$$C_{25}H_{18}NCl + Zn + HCl = C_{25}H_{18}NH + ZnCl_2,$$
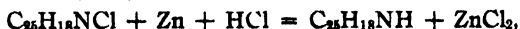
the acid necessary for the reaction coming from slight hydrolysis of the chloride;

$$C_{25}H_{18}NCl + H_2O = C_{25}H_{18}NOH + HCl.$$
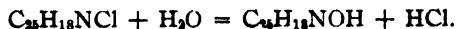
The formation of diphenylacridane is, however, only a minor reaction. The major part of the acridyl salt simply gives up its acid radical and forms the free acridyl radical. Out of the reaction between 4 g. of the acridyl sulfate and zinc dust, only about 0.1 g. of the acridane has been isolated. The diphenylacridane is very soluble in benzene so it will be found in the benzene-petroleum ether mother liquors from which the free radical diphenylacridyl has been crystallized. These mother liquors are allowed to evaporate to dryness and the dark residue extracted with hot ligroin, boiling between 80° and 90°. The residue remaining after evaporating the ligroin is treated with a small amount of alcohol acidulated with hydrochloric acid to remove acridol and peroxide. The insoluble portion, after cooling the alcohol, is diphenylacridane. This is recrystallized from ligroin, from which it separates as almost perfect cubes with a high re-

fractive index, melting point 175.°. On standing in the air, the crystals assume a slight yellow tinge.

Diphenylacridane can also be prepared by adding zinc dust to a boiling solution of diphenylacridol in acetic acid. The free radical, diphenylacridyl, is formed as an intermediate product, as is shown by the instantaneous production of a deep red color on adding the zinc dust. If the boiling is continued for some time with the occasional addition of zinc dust to the acid solution, the red color will be gradually discharged to a pale yellow. On pouring the acetic acid solution into water acidulated with hydrochloric acid, the diphenylacridane precipitates as colorless flakes. These, on drying and recrystallizing from ligroin, show the same properties as given above.

> Calc for $C_{18}H_{19}N \cdot$ C, 90 04; H, 5 75; found· 89 75 and 6 00
>
> Molecular weight: Calculated, 333; found: 331 in boiling chloroform

Analogues of Diphenylacridyl.—The following analogues of diphenylacridol have been prepared and from them, salts, free radicals and peroxides, have been obtained. *p*-chlorophenyl-*N*-phenylacridol, *p*-methoxyphenyl-*N*-phenylacridol, 2,4-dimethoxyphenyl-*N*-phenylacridol, phenyl-*N*-methyl acridol, phenyl-*N*-ethylacridol. So far as studied, the salts of all of these acridols behave essentially as do the salts of diphenylacridol. In each case the watery solutions of the salts give a free, dark brownish red radical with zinc dust. All of these free radicals are soluble in benzene and in solution are readily oxidized to form peroxides. The salts having aliphatic radicals attached to the nitrogen atom tend to yield more of the acridane and less of the free radical than the aryl nitrogen acridyl salts. The free radicals and the peroxides obtained above will be described in the next paper.

ANN ARBOR, MICH

THE PREPARATION OF RAFFINOSE.

BY C. S. HUDSON AND T. S. HARDING.[1]

Received August 4, 1914.

In the course of an investigation on the hydrolysis of raffinose by enzymes, it became necessary to prepare several kilograms of the sugar. A method which was devised for the purpose has proved materially preferable to the procedures recorded in the literature and its description may be useful to those requiring a supply of raffinose.

Selection of the Best Natural Source for Raffinose.

It is recorded that crystalline raffinose has been isolated from Australian

eucalyptus manna,[1] cottonseed,[2] beet molasses,[3] barley,[4] wheat,[5] and the leaves of the yew[6] (*Taxus baccata* L.). The crystallization of raffinose from eucalyptus manna appears to have been readily accomplished, and with as high a yield as 60%, but we are informed by correspondents in Australia[7] that the manna is difficult to obtain in quantity. Beet molasses, barley, and wheat, though easily obtained, contain considerable quantities of sugars other than raffinose and in consequence its crystallization from these sources is difficult and the yield small. The yield of raffinose from the leaves of the yew appears to be very small. On the other hand, cottonseed is a very satisfactory source because it is readily obtained, is inexpensive, contains several per cent. of raffinose and does not contain other sugars or interfering substances in sufficient proportion to prevent a rapid crystallization of the raffinose from the purified and concentrated extract of the seed. Upon inquiry of manufacturers, we learn that most of the raffinose which is prepared for the chemical market is made from this natural source.

Cottonseed can best be used for this preparation in the form of cottonseed meal, which is the ground press cake that remains after the oil has been expressed from the hulled seed. Cottonseed meal is extensively used as a cattle food and fertilizer and may be purchased from feed merchants.

Methods of Ritthausen and of Zitkowski for Preparing Raffinose from Cottonseed Meal.

Ritthausen was able to obtain a yield of from 1 to 2 5% of crystalline raffinose from cottonseed meal by extracting the latter with warm 80% alcohol, evaporating the solvent, extracting coloring matter and oil from the residue with ether, precipitating impurities from the aqueous solution of the residue with lead acetate, removing the excess lead as sulfide, and concentrating the solution to a syrup, which crystallized on keeping at about zero during one or two weeks. When this process is carried out on a large laboratory scale, it has been our experience that it is expensive and inconvenient, on account of the extractions with alcohol and ether. The yield is also unsatisfactory because cottonseed meal contains on the average 6–8% of raffinose, judging from the polarimetric reading of the extract.

[1] Johnston, *Phil Mag*, **23**, 14 (1843), Berthelot, *Ann chim phys*, **46**, 66 (1856), Tollens, *Ber*, **18**, 2611 (1885), Passmore, *Pharm J Trans*, **21**, 717 (1890)

[2] Ritthausen, *J prakt Chem*, **29**, 391 (1884), Böhn, *Archiv pharm*, [3] **22**, 159 (1884)

[3] Loiseau, *Compt rend*, **82**, 1058 (1876).

[4] O'Sullivan, *J Chem Soc*., **49**, 70 (1886).

[5] Schulze and Frankfurt, *Ber*., **27**, 64 (1894)

[6] Hérissey and Lefebvre, *J pharm Chim*, [6] **26**, 56 (1907)

[7] Anderson & Co, Ltd, Seedsmen, of Sydney, New South Wales

Zitkowski[1] has prepared raffinose from cottonseed meal by extracting the latter with water, pressing the extract from the meal, making it alkaline with lime and filtering, precipitating the raffinose at a low temperature in a special cooling and stirring apparatus with powdered lime, and regenerating the raffinose from its insoluble lime compound by carbonating. After evaporation to a syrup, there slowly crystallized at a low temperature about 0.8% of raffinose. Although this method avoids extractions with alcohol or ether, the yield is very low, and in repeating the process, it has been our experience that it is difficult to carry out, though we succeeded in obtaining a yield of about 1% of low grade raffinose.

An Improved Method for Crystallizing Raffinose from Cottonseed Meal.

The following is a description of a procedure by which we have prepared, in the laboratory at different times, about 5 kilograms of raffinose from various samples of commercial cottonseed meal with a yield of 2.5 to 4%.

One kilo of meal is mixed with 5 liters of tap water and filtered with suction on a large Büchner funnel as quickly as possible, because a delay of fifteen minutes or more may cause the meal to become too slimy for filtration. The sugar contained in the meal dissolves very readily in cold water and the meal may be washed on the funnel with cold water until the filtrate shows no optical rotation. To the combined filtrates there is added the usual basic lead acetate solution[2] in slight excess, which requires about 1 cc. for each 5 g. of meal. The yellow lead precipitate is removed by slow filtration over night through paper[3] and is washed in the morning, after transference to a Büchner funnel, until the washings show no rotation. The combined filtrates should be brilliantly clear and of a light yellow color. The excess of lead is next removed as lead sulfide, after saturating with hydrogen sulfide gas. It will be found that the filtrate is slightly acid and is colorless, but regains its yellow tint if made alkaline, showing that the color is due to a natural indicator. A measurement of the optical rotation and volume of the solution at this stage will indicate the presence of about 80 g. of raffinose (anhydrous $C_{18}H_{32}O_{16}$, specific rotation $[\alpha]_D = +123$), on the assumption that the rotation is due only to raffinose. In support of this assumption, it may be said that reducing sugars are present only in traces and no sugar except raffinose has so far been detected. There is then added to the solution about 0.2 g. of sodium hydrosulfite[4] to prevent development of color and it is boiled under reduced pressure in glass to a syrup of about 25% water content, which should have no more than a slight yellowish color.

[1] "American Sugar Industry," Sept, 1910, page 324.

[2] Prepared, for example, according to the directions in U. S. Dept. Agr, Bur Chem, *Bull* 107, p 40, or Browne, "Handbook of Sugar Analysis," p. 208.

[3] In working with large quantities, it would probably be advantageous to use a bag filter

[4] See Browne, "Handbook of Sugar Analysis," p. 221.

It has proved very advantageous at this stage to follow a modification of the procedure of Gunning[1] in the preparation of barium raffinosate. Barium hydroxide is added to the syrup in the proportion of 2 g. of the octahydrate to each gram of raffinose and the solution is completed by warming to not over 80° for a few minutes, fifteen usually being sufficient. The mixture is gradually poured into one and a half times its volume of anhydrous methyl alcohol[2] contained in a large mortar, and the barium raffinosate, which precipitates as a granular compound, is ground to a fine powder, filtered off, and washed with methyl alcohol. Ethyl alcohol (95%) has been successfully used in place of methyl for the precipitation of this compound but it comes down more quickly and cleanly and is more readily decomposed later if methyl alcohol is used. The barium compound is suspended in about 1500 cc. of distilled water and decomposed by the gradual addition of 50% phosphoric acid solution, care being taken to reach exact neutrality at the end of the process. The voluminous precipitate of barium phosphate is filtered off with suction and is thoroughly washed until the filtrate has no rotation. The solution should be of a light yellowish brown color at this stage. Since the barium phosphate is slightly soluble, it has been found necessary to precipitate the last traces of barium with sulfuric acid and filter. A redetermination of the volume and optical rotation of the solution at this stage will show the extent to which the raffinose has been recovered from the barium compound. With ordinary precautions, the yield is 95% of the theoretical but yields of 98–99% are not unusual. Fifty grams of eponite[3] are mixed with the solution and the latter is filtered in a few minutes, since little advantage results from long standing or heating. The filtrate is still yellow in color, which, however, does not interfere with subsequent crystallization. The solution is next boiled *in vacuo* to a light straw colored syrup of about 20 to 25% water content and there is added just to saturation 95% ethyl alcohol, containing 0.3% nitric acid, about 10 to 15 cc. being usually required. This acidification of the alcohol has proved useful for the purpose of avoiding high ash content in the crystalline raffinose. The mixture is then seeded with crystals of raffinose hydrate and set away at 0° to crystallize over night. In the morning the solid mass of crystals is ground with 75% ethyl alcohol in a mortar, filtered off with suction, and washed with the same strength alcohol until the washings are colorless. The yield is about 40 g. of colorless raffinose crystals, and it may be increased 10 g. by working over the mother liquor a second time through the barium hydroxide purification. The chief impurity in this raffinose is an ash

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[1] *Bull. de l'association Belge de chim.*, **4**, 318 (1890).

[2] A commercial anhydrous grade which may be purchased for about eighty cents per gallon.

[3] A recently introduced vegetable carbon of high purifying power which may be purchased of dealers in chemical supplies.

content of 0.5 to 1% which may be removed by recrystallization. For this purpose a 50% aqueous solution of the crystals is prepared, filtered, and to it is added the previously mentioned acidified alcohol, nearly to cloudiness, and the solution stirred. Crystallization of raffinose hydrate is rapid at room temperature and the crystals, which may be washed first with 75% and later with 95% alcohol, contain less than 0.05% ash, give a specific rotation of 123.2° (anhydrous sugar) in 10% aqueous solution at 20°, and the yield is about 2.5% of the weight of the original meal. A further crystallization of 0.5% of equally pure raffinose may be obtained by cooling the mother liquor to zero.

BUREAU OF CHEMISTRY,
DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE OCCURRENCE OF METHYL ALCOHOL IN CORN SILAGE.

BY E. B. HART AND A. R. LAMB
Received August 4, 1914.

In 1912, Hart and Willaman published a paper on the volatile fatty acids and alcohols of corn silage.[1] From the data secured in the separation of the alcohols by the Duclaux method, it was concluded that corn silage contains, besides ethyl and propyl alcohols, a small amount of methyl alcohol. The quantity found may be approximately expressed as 0.05% of the silage mass, or about 20 g. in 100 pounds of silage.

In the same year there appeared a paper by Dox and Neidig,[2] in which the main conclusions of Hart and Willaman were substantiated, but which did not agree on the presence of methyl alcohol. The question of the occurrence of methyl alcohol in corn silage is therefore taken up in this paper.

Experimental Part.

There are numerous methods in the literature, of varying degrees of reliability, for the detection of methyl in the presence of ethyl alcohol. Many of these were tested with various known mixtures of alcohols, and only those which appeared always to be trustworthy were used. Of these, the Trillat test,[3] and the resorcin test, as modified by Scudder,[4] seemed to be most reliable. The gallic acid test,[5] the morphine test,[6] the phenol test,[7] the Haigh phloroglucin test, which is discussed by Scudder,[8] and

[1] THIS JOURNAL, 34, 1619 (1912).
[2] Research Bull. 7, Iowa Expt. Sta.
[3] Bull. 107, Bureau of Chem., p. 99.
[4] THIS JOURNAL, 27, 892.
[5] Ann. de Chim. analyt. appl., 4, 156 (1899).
[6] Hinkel, Analyst, 33, 417.
[7] Leach, "Food Inspection and Analysis," 2d ed., p. 820.
[8] Loc. cit.

the Sanglé-Ferriére-Cumiasse test, as modified by Scudder and Riggs,[1] were used as confirmatory tests. A number of the most trustworthy tests for methyl alcohol have been thoroughly tried out by Scudder,[2] and his conclusions as to the reliability of the tests and proper conditions for their use have been substantiated in this work.

The following method was used in demonstrating the presence of methyl alcohol in normal corn silage: About 300-400 g. of silage were comminuted in a food grinder, suspended in water, and distilled with steam. The first sample was distilled at atmospheric pressure, but the later ones were distilled under reduced pressure at from 30-40 mm., to eliminate the possibility of chemical changes taking place at the higher temperature. Only about one liter was usually distilled over, thus getting less than half of the volatile acids and alcohols in the distillate, as was determined by titrating the distillate and the total acidity, and comparing with the average acidity of normal silage, as determined by Hart and Willaman. The distillate, having been neutralized with NaOH, was redistilled, also under reduced pressure, to liberate the alcohols, and the distillate containing the alcohols concentrated by repeated distillation, with the aid of a fractionating column. In each case, the samples were distilled, and the distillates concentrated uniformly, so that the results of the tests could be compared. In one case a water extract was made, by grinding up a sample of about 400 g., triturating in a mortar, and filtering rapidly on a Buchner funnel. The filtrate, about 1.5 liters, was distilled in steam under reduced pressure, neutralized, and redistilled as above. Table I shows the results of the tests made on each sample.

TABLE I.—RECORD OF TESTS FOR METHYL ALCOHOL IN NORMAL CORN SILAGE.

Sample.	Temp of dist	Resorcin test.	Triflat test	Phenol test	Gallic test	Haigh test	Morphine test	Sanglé-Perriére-Cumiasse
1 Stave silo	100°	+	+	+				
2 Stave silo	35°		+ (strong)					
3 Stave silo	30°	+ (strong)	+	+		+		.
4 Stave silo water extract	28°	+	+ (very strong)	+ (strong)				
5 Concrete silo .	40°	+ (*very strong*)	+	+	+		+	+

The presence of methyl alcohol in normal silage having been established,

[1] THIS JOURNAL, **28**, 1202 (1906).
[2] *Ibid.*, **27**, 892 (1905).

an attempt was made to determine the source of it.   F. Ehrlich has shown[1] that certain yeasts have the power of fermenting amino acids with the formation of the corresponding alcohols, as in the following equation

$$R.CHNH_2.COOH + H_2O = R.CH_2OH + CO_2 + NH_3$$

He has further shown that one of the specific sources of methyl alcohol in a protein-carrying fermentation mixture is glycine, as shown by the following equation·

$$CH_2NH_2.COOH + H_2O = CH_3OH + CO_2 + NH_3$$
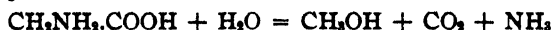
To determine whether or not the methyl alcohol in normal silage has its source in the glycine of the corn proteins, a number of water cultures with synthetic media were set up and inoculated with a small piece of normal silage, obtained under antiseptic conditions from the large concrete silo on the University farm, the sample being taken about two feet below the surface of the silage   A typical medium was composed as follows

CaCO₃	1 g
K₂HPO₄	1 g
MgSO₄	0 1 g
FeCl₃	Trace
NaCl	Trace
Glucose ..	2 g
Glycine	2 g
Distilled water .	1 liter

The object of this method of inoculation was to carry into the cultures all of the typical silage flora.   These cultures were arranged, according to the composition of the media, into pairs, each pair being similar in composition, except that one contained glycine as the sole source of nitrogen, and the other some other nitrogenous substance   All contained either glucose or a tartrate as the source of carbon, except cultures I and II, which con-

TABLE II —TESTS FOR METHYL ALCOHOL IN WATER CULTURES.

Cultures		Resorcin test	Trillat test	Phenol test	Gallic acid test	Sanglé-Ferriére-Cumiasse
I.	Glycine	+	+	+	+	+
II.	Glycine	+ (strong)				
III	Glycine	+	—			
IV	No glycine	—	—			
VII	Glycine	—				
VIII	No glycine	No growth				
IX	Glycine	+			+	+
X	Glycine	+ (strong)				
XI	No glycine	+ (weak)				
XII	Glycine	+		+		+

[1] *Wochschr Brau* , 30, 561, *Z angew Chem.*, 27, 48 (1914).

tained only glycine and inorganic salts. Considerable growth and formation of methyl alcohol was obtained even in these two cultures. Moreover, no other organic substance which might be fermented to methyl alcohol was present. After being allowed to stand at room temperature for three or four weeks, the cultures were distilled in steam, at ordinary pressure, and the distillates concentrated and tested for methyl alcohol. The results, which are shown in Table II, seem to indicate the possibility of glycine being at least one of the sources of the methyl alcohol.

The objection, however, may be justly raised, that under different conditions of environment, the flora of the silo might not be typically represented in these cultures. To secure more definite evidence, silage was made in the laboratory, in sealed jars, using corn which had been grown to maturity in the greenhouse. Jar No. 1 contained normal silage, jar No 2 contained normal silage to which a solution containing 2 g. of glycine had been added, and jar No. 3 normal silage to which 2 g. of glycine and 50 cc of ether had been added. The silage in these jars was excellent, and was perfectly normal in appearance, odor, taste, and acidity, except that in jar No. 3 the ether had inhibited the action of organisms, and there was much less acidity developed. Otherwise the silage in this jar had practically the same appearance and odor as that in the others, after the ether had been allowed to evaporate. During the ripening of the silage, the pressure of gas was relieved at intervals by opening a pinchcock. Considerably less gas was developed in jar No. 3 than in the others.

At the end of about six weeks samples of 350 g. were ground and distilled as in the case of the normal silage. The titer of volatile and fixed acid was practically the same, in jars No. 1 and No. 2, the total acidity being equivalent to about 225 cc. of 0.1 N alkali per 100 g. of silage, but the total acidity in jar No. 3 was only about one-third as great as in the other two. The alcohols were distilled off, concentrated somewhat, and the tests for methyl alcohol applied, with the results as shown in Table III.

TABLE III —TESTS FOR METHYL ALCOHOL IN EXPERIMENTAL SILAGE

Sample	Temp of dist C	Resorcin test	Trillat test	Phenol test	Gallic acid	Haigh test	Morphine test
1 Normal silage	35°	+ (weak)	+ (very weak)	+	+ '	+	+ (very weak)
2 Glycine silage..	40°	+ (very strong)	+ (strong)	+ (strong)	+	⊥	+ (strong)
3 Glycine-ether silage	40°	—	—	—	—		—

From the data shown, it is evident that more methyl alcohol was formed in the silage to which glycine had been added, which fact supports the hypothesis that its source is the glycine. In these two jars, the experimental conditions were exactly the same throughout, except the addition

of the glycine, and the consequent increase in the amount of methyl alcohol formed. The difference in the strength of the tests, as indicated in the table, was very pronounced. The fact that in jar No. 3, the silage which ripened in the presence of an antiseptic contained no trace of methyl alcohol, even though a similar amount of glycine had been added, seems to show that the formation of this alcohol is brought about by some organism. This is in harmony with the results secured from the water cultures.

Of course, at this stage of the work, we can point, with certainty, only to the presence of an appreciable amount of methyl alcohol in normal silage, and merely indicate the probability of its formation by the hydrolysis of glycine. It is also possible that other substances than glycine may furnish some methyl alcohol in the presence of certain organisms, as for example, the fermentation of glycerine by B. Boöcopricus.[1] Indeed, the presence of methyl alcohol in fermentation mixtures is not new. Wolff[2] found it present in the distillate from fermented fruits, such as apples, cherries, grapes, and plums. Sanglé-Ferriére and Cumiasse[3] found it in absinthe. Takahashi[4] discovered methyl alcohol among the products produced by several varieties of mycoderma yeasts in fermenting rice mixtures. Evidently a number of different species of microörganisms possess the power of producing methyl alcohol in fermenting mixtures.

Summary.

Normal silage is shown to contain small amounts of methyl alcohol. A number of tests were made on the distillates from several samples of silage, the tests having first been standardized by using various known mixtures of alcohols. The number of different tests used precludes the possibility of positive reactions being given by some other substance than methyl alcohol.

The hypothesis is advanced that at least part of the methyl alcohol is formed by the action of microörganisms on glycine. All work done thus far with water cultures and experimental silage shows results which support that hypothesis.

MADISON, WIS

THE VOLATILE SUBSTANCES OF URINE.

BY WILLIAM M. DEHN AND FRANK A. HARTMAN.

Freshly voided, normal urines possess low vapor pressures[5] and little odor, thus indicating the presence of only traces of volatile substances.

[1] Emmerling, Ber., 29, 2726.

[2] Compt. rend., 131, 1323.

[3] Ann. chim. analyst, 8, 82 (1903).

[4] Bull. Coll Agr. (Tokyo), 6, 387 (1905).

[5] Vide infra

After standing, all urines undergo bacterial changes,[1] develop increased vapor pressures and give off disagreeable odors, thus indicating *decompositions of complex nonvolatile molecules contained in the fresh urines.* These decompositions are indicated not only in the fermentation of urines, but also in the results of evaporation[2] to dryness and ignition   The latter operations develop from the nearly odorless fresh urines intolerably nauseating odors which evidently were not present in the originals   Furthermore, as will be shown below these characteristic odors may easily be developed by the hydrolytic action of dilute acids and alkalies   Thus we have various conditions and operations intensifying the odors of urine, and the conclusion is inevitable that *these disagreeable volatile substances were not present as such in the original urines but were produced by hydrolysis, reduction, oxidation or splitting of complex conjugated compounds contained therein*   Such odor-poducing, conjugated compounds, except in cases of urea, phenol and indol, have not been described in the literature, at least the antecedents of some of the odorous compound of urine seems to have been overlooked by previous investigators.

Studies, first undertaken three years ago to determine these odoriferous substances, have not only confirmed the view that numerous hitherto known volatile substances are present in urine but also have developed the view that no small number of hitherto unknown substances also are present.   Some of the latter have now been studied and others are being investigated.

Since no systematic study of volatile substances of urine has been made, it is purposed to make such studies both of freshly voided urine and urines treated with bacteria, acids and alkalies   These studies are undertaken to determine.

1. The volatile substances of urine.
2. The cause of the characteristic odor of urine.
3. The toxic constituents of urine.
4. The molecular forms of conjugated, deodorized, detoxified substances of urine.
5. The influence of the antecedents of such compounds on metabolism.

A large number of volatile substances contained in urines have been described in the literature.   These have been classified as

[1] THIS JOURNAL, 36, 410 (1914)

[2] Van Nuys, "The Chemical Analysis of Healthy and Diseased Urine," 1888, p. 10   "The chemical constitution of the body to which urine owes its odor is not known.   It volatilizes very slowly, as urine does not lose all of its odor by boiling or evaporation."

[3] Long, "Urine Analysis," 1900, p 13   "Normal urine contains traces of complex aromatic bodies, the exact nature of which cannot in all cases be given "

1. Normal physiological constituents.
2. Casual physiological constituents.
3. Pathological constituents.

However, since these run one into the other, since it is sufficiently important to recognize *what* substances can be eliminated by the kidneys, and since our method of study is based on *chemical differences*, the following classification of volatile substances of urine is made.

TABLE I.—VOLATILE SUBSTANCES OF URINE.

Acids.		Phenols.	
Normal	Abnormal.	Normal	Abnormal.
Carbonic	Aceto-acetic	Phenol	Catechol
Formic	β-Hydroxybutyric	p-Cresol	Naphthol, etc
Acetic	Valeric	Other phenols	
Propionic	Levulinic		
Butyric	Crotonic		
Benzoic	Phenylacetic		
Other acids			

Bases.		Neutral substances.	
Normal.	Abnormal.	Normal.	Abnormal
Ammonia	Pyridine	Oxygen	Acetone
Methylamine	Trimethylamine	Nitrogen	Ethyl sulfide
Indol[1]	Benzylamine, etc.	Hydrogen peroxide	Methyl mercaptan
Skatol		Urinol hydrosulfide	Alcohol
		Other compounds	Terpenes, etc.

This classification does not assume that the listed substances are invariably found in the urine or that when eliminated by the kidney they are found in the urine in the molecular forms indicated, for it must be remembered that usually it is impossible to observe when uriniferous substances hydrolyze or split into their more simple molecules.

Furthermore, no claim is made that the table includes all of the volatile substances hitherto recognized. It merely suffices to show that *hitherto known substances*[2] *do not produce all the uriniferous odors;* these must be sought for among hitherto undetected substances.

Other substances which either have not been definitely established, or have had their origin from foods and therapeutically administered materials, have been omitted from the list.

Acid Volatile Substances.

When the odor of urine is mentioned in the literature it is vaguely de-

[1] Though indol is a weak base, in the method of separation described below, it appears among the neutral substances.

[2] The words *component* and *constituent* as defined by some authors to designate *mixture* and *compound* cannot be applied to the volatile substances of urine without ambiguity. At first many of the volatile substances are conjugated hence may be termed constituents, but after hydrolysis, they may be termed components. The less-limiting word *substance* is used in this paper.

scribed as being caused by volatile acids. Moreover, the usual acidity of urines is attributed, at least partially, to various organic acids. It is well, therefore, to note what acids are present and here especially to consider what acids may contribute to the odor   However, as will be shown, none of the listed acids possess odors likely to be mistaken for the characteristic odor of urine   Carbonic[1] and benzoic acids are odorless   The lower fatty acids[2] occur in small quantities and, except under rare pathological conditions, are present as salts or in conjugated forms, hence are not appreciably contributory to the odor of urines   It must be added that, in fermenting urines, volatile acids are increased at the expense of carbohydrates,[3] present

The occurrence of hydrogen sulfide has been observed by various investigators [4]   Salkowski considered that its evolution from urine is to be traced to the action of bacteria on neutral sulfur compounds, as sulfates or thiosulfates   Karplus[5] also observed bacterial formation of hydrogen sulfide in urines   We have observed that *all urines slowly give off hydrogen sulfide* when treated with cold, dilute phosphoric or sulfuric acid   An explanation of this will be made in connection with *urinod* [6]

Acetoacetic and β-hydroxybutyric acids[7] are both contributory to the pleasant odor of diabetic urines   Levulinic,[8] crotonic[9] and phenylacetic acid have also been reported

[1] Winter and Schmidt   *Centr physiol*, 1, 421, Marchand   *J prakt Chem*, 44, 250

[2] For summary of early literature, see Jaksch   *Z physiol Chem*   10, 536, for other literature see Dakin's "Oxidation and Reductions in the Animal Body   (Monographs on Biochemistry), 1910, pp 113–16, see also Magnus, *Z Med*, 73, 428, Molnar, *Z exp Path*, 7, 343, Strisower *Biochem Z*, 54, 189, Thudichum, *J Chem Soc*, 23, 400, Pfluger's, *Arch Physiol*   15, 12, Stadeler, *Ann chem Pharm*, 77, 17, THIS JOURNAL, 8, 86

[3] Salkowski, *Z physiol Chem*, 13, 264, *J Chem Soc*, 23, 400.

[4] Salkowski, *Berl klin Woch*, 25, 722, *Chem Zentr*, 1888, 1471, Porcher and Havieux, *Compt rend soc biol*, 68, 27

[5] Karplus, Virchow's *Arch*, 131, 210, see also Sasaki and Otsuka, *Biochem Z*, 39, 208

[6] See following contribution

[7] For literature on these acids see Dakin's bibliography quoted above   See also Duchmuller, Szymanski and Tollens, *Ann*, 228, 92, Minkowski, *Chem Zentr* 1884, 406, Wolpe, *Ibid*, 1887, p 277, Stadelmann, *Z Biol*, 32, 456, Klinger, *Ann Chem. Pharm*, 106, 18, Neubauer, *Ibid*, 97, 129, *J Pharm chim*, [3] 29, 320, Araki, *Z physiol Chem* 18, 1; Magnus, *Arch exp Path Pharm*, 42, 149, Hilger, *Ann*, 195, 314

[8] Weinstraud, *Chem Zentr*, 1895, p 292

[9] Stadelmann, *Z Biol*, 21, 140, Salkowski, *Z physiol Chem*, 7, 450, 9, 8, Araki, *Ibid*, 18, 1

Phenolic Volatile Substances.

A large number of simple and polyhydric phenols[1] and their derivatives may appear in the urine conjugated either with sulfuric acid or glucuronic acid. For our study here, phenol and p-cresol are the most important, since they are odorous, volatile and appear in the largest quantities, as may be seen in the following experiment·

One thousand liters of urine were treated with dilute sulfuric acid and distilled, the distillate gave, by methods described below, phenols of the following fractions:

			Grams			B p
(1)	170°	about	1 34		phenol	183°
(2)	170-200°		19 13		p cresol	202°
(3)	200-230°		8 12		thymol	232°
(4)	230-260°		0 67	Compare with	catechol	240°
(5)	260-320°		2 45		resorcinol	276°
					α naphthol	282°
		Total,	31 71		β naphthol	288°

It need only be observed here that the odors of phenols do not give the characteristic odor of urine.

Basic Volatile Substances.

Ammonia[2] is the most important base positively known to occur in urine. During the hydrolysis of urea in fermenting urines, ammonium carbonate is formed in large quantities—this decomposes into free ammonia which almost universally has been mistaken for the characteristic odor-producing substance of urine Although ammonia contributes to the disagreeable odor of alkaline urines, such contribution is only secondary, as may be easily proven by the experiment of heating urines with dilute sulfuric acid— this retains the ammonia but liberates the uriniferous odor.

The occurrence in urine of methylamine,[3] trimethylamine[4] and other

[1] For bibliography of phenols see Dakin's *Loc cit* **1910**, p 130 Baumann, *Ber* , **9**, 54, 1389, 1715, 1747, **10**, 685, **11**, 1907, **12**, 2166, Pfluger's *Arch* , **12**, 63 69, **69**, 285, *Z physiol Chem* , **1**, 60, **2**, 335, **10**, 123, Monfet, *Compt rend* , **137**, 386, Salkowski, *Ber* , **9**, 1595, **10**, 842, Labby and Vitry, *Compt rend soc biol* , **62**, 699 For quantities of phenols in urines see Rumpf, *Z physiol Chem* , **16**, 220, Neuberg, *Ibid* , **28**, 123, Mooser, *Ibid* , **63**, 155 For naphthol in urine see Edlefsen, *Chem Zentr* , **1905**, p. 1341, Desesquelle, *Compt rend soc biol* , [9] **2**, 101 For catechol, see Baumann, Pfluger's *Arch Physiol* , **12**, 63, Moscatelli Virchow's *Arch* , **128**, 181

[2] Neubauer, *J prakt Chem* , **64**, 177, 279 Salkowski and Munk Virchow's *Arch*, **71**, 500, Rumpf, *Ibid* , **143**, 1, Salkowski, *Z physiol Chem* , **1**, 26, Gumlich, *Ibid* , **16**, 19, Rumpf and Kleine, *Z Biol* , **39**, Jubelband, 65, Camerer, *Ibid* , **43**, 13, Tidy, Meymott and Woodman, *Proc Roy Soc* , **20**, 362, Folin, *Am J Physiol* **13**, 45, 66, Grafe and Schlaffer, *Z physiol Chem* , **77**, 1, Wills and Hawk *J Biol Chem* , **9**, 30, Boussingault, *Ann chim phys·* [3] **29**, 472, Heintz, *J prakt Chem* **64**, 399, Hallerwarden, Virchow's *Arch* **143**, 705

[3] Schiffer, *Z physiol Chem* , **4**, 237, Erdmann *J Biol Chem* , **9**, 85, Folin, *Ibid* , **3**, 83, Takeda, Pfluger's *Arch* , **129**, 82, Schmiedeberg, *Arch exp Path Pharm* , **8**, 1

[4] de Filippi, *Z physiol Chem* , **49**, 433, Erdmann, *J Biol Chem* , **8**, 57, **9**, 85; Dessaignes, *Compt rend* , **43**, 670, Takeda, Pfluger's *Archiv* , **129**, 82

aliphatic amines has not definitely been established.   Indol and skatol[1] are excreted in chemical combination with sulfuric or glucuronic acids. Pyridine[2] and benzylamine[3] have been reported in rare cases.

Neutral Volatile Substances.

This division, including *urinod*, and at least two other new and closely related substances, will be shown to contribute the most important volatile substances of urine.

Oxygen, nitrogen and hydrogen peroxide, possessing no odors, are unimportant in this discussion.

Acetone,[4] one of the most important and most investigated substances of pathological urines, contributes to the aromatic odor of diabetic urines.

Ethyl alcohol[5] sometimes appears in the urine of diabetics.   It is also of interest to know that a small portion of the alcohol of imbibed beverages[6] is eliminated in urine either in the free or the combined form.

Other neutral volatile substances which have been reported as present in urine under special conditions are chloroform,[7] iodoform, ethyl sulfide,[8] methyl mercaptan[9] and the terpenes.

From the foregoing discussion it may be concluded that the volatile substances hitherto known to be present in urine are not responsible for its characteristic odor.   Though some of these are contributory to it, the following experiments will show that the newly discovered substance *urinod*[10] is the *id ipsum* of the odor of urine.

[1] For voluminous bibliographies on indol and skatol see Hammarsten's physiological chemistries   A regular occurrence of indol in the distillate of normal urine is maintained by Jaffe, *Arch exp Path Pharm* , Suppl , **1908**, p 299

[2] Kutscher and Lohmann, *Z Nahr Genussm* , **13**, 177

[3] Schmiedeberg, *Arch exp Path Pharm* , **8**, 1, **14**, 288, 306, Mosso, *Ibid* , **26**, 267.

[4] For voluminous bibliographies on acetone see (a) Huppert-Neubauer, *Harn-Analyse*, 10 Aufl , (b) v Noorden's *Lehrb d Pathol des Stoffwechsels*, Berlin, 1893, (c) Dakin's "Oxidations and Reductions in the Animal Body" (Monographs of Biochemistry), **1912**, pp 113–116, also see Jaksch, *Z physiol Chem* , **6**, 541, Muller, *Berl klin Woch* , **1887**; *Chem Zentr* , **1907**, p 366, Jagerroos Bjorneborg, *Arch Gyn* , **94**, No 2, Piper, *Lancet*, **185**, 535, 602, Wallace and Gillespie, *Practitioner*, **84**, 2, Abram. *J, Path Bact* , **3**, 420

[5] Markownikoff, *Ann* , **182**, 362, Pohl, *Arch exp Path Pharm* , **31**, 281, Voltz, Baudrexel and Dietrich, *Arch ges physiol* , **145**, 210, Dupré, *Proc Roy Soc* , **20**, 268; Béchamp, *Compt rend* , **75**, 1830, Maignon, *Ibid* , **140**, 1063, 1124

[6] Dupré, *Proc Roy Soc* , **20**, 268, Voltz and Baudrexel, *Arch ges Physiol* , **142**, 47, **145**, 210

[7] Vitali, *L'Orosi* 16, 299, Nicloux, *J pharm chim* , [6] **24**, 64

[8] Neuberg and Grosser, *Chem Zentr* , **2**, 835 Abel, *Z physiol Chem* , **20**, 253

[9] Karplus, Virchow's *Arch* , **131**, 210

[10] Moor described a substance obtained from the residue of urine by extracting with alcohol   He called it *urene*   It was shown by Gies and Haskins to be a mixture containing large quantities of urochrome   Moor, *Z Biol* , **44**, 123, **45**, 420, *Med. Record*, **58**, 336, 471, *Le physiologiste russe*, **2**, 128, 131, Gies, *Med Record*, **59**, 329; THIS JOURNAL, **25**, 1295 (**1903**), Haskins, *Am J Physiol* , **12**, 162   It probably contained traces of *urinod hydrosulfide*, as will be shown below.

Experimental Part.

Preliminary studies were made on the vapor pressures and the volatile acidities of normal urine. Our important experimental results, however, were obtained by hydrolysis and distillation of urines with dilute sulfuric acid.

Vapor Pressures of Normal Urines.

Vapor pressure determinations[1] were made under the following indicated conditions.

Sample	Age Hours	Temperature	Vapor pressure of Urine	Vapor pressure of Water	Difference	Remarks
A	1	24 0	12 2	22 2	10 0	Acid reaction
A	67	21 8	16 4	19 5	3 1	Acid reaction
A	120	23 0	19 3	20 9	1 6	Acid reaction
A	504	23 0	16 4	20 9	4 5	Containing mold
B	13	20 2	13 4	17 6	4 2	Acid reaction
B	60	21 6	15 9	19 0	3 9	Alkaline reaction
C	0 1	20 5	16 6	18 0	1 4	Acid reaction
C	3 2	21 1	11 0	18 7	7 7	Acid reaction
C	24 0	20 3	10 8	17 7	6 9	Alkaline reaction
C	30 0	20 8	15 5	18 4	2 9	Alkaline reaction

It is observed that the vapor pressures (1) are not constant throughout the times observed, (2) their variations are not large; and (3) they are lower than aqueous pressures at the same temperature. Since many chemical reactions are going on in urine, involving fermentation, hydrolysis, oxidation, reduction, etc., especially developing ammonium carbonate from urea and multiplying the oxygen-consuming bacteria—it is to be expected that disturbances of the vapor pressure equilibria will result shortly after the urine is voided, and will continue until all fermentations cease. Since the reaction products may have opposite effects upon the original vapor pressure, the equilibrium may not be disturbed or may be disturbed only slightly, therefore, such determinations may have little or no value. For our purpose they show that no large quantity of easily volatile substances is present in normal urine.

Volatile Acidity of Urine.

Since the odor of urine is often judged to be caused by "volatile aromatic acids" it was considered of importance to measure such volatile acidity. Air was, therefore, drawn through a series of bottles supplied with Folin's aspiration tubes. The first bottles contained appropriate solutions for fixing atmospheric acids and bases; next followed the bottle containing the urine; and finally the bottle containing 0.1 N alkali. Thus the acids, volatile at ordinary temperature, were carried over into the alkali and the loss of alkalinity was measured.

Fresh urines and fermented urines were tested in this manner; both were

[1] For method employed see THIS JOURNAL, **29**, 1052 (1907)

aspirated directly or after treating with dilute sulfuric acid to liberate free acids from their various combinations.

Sample	Volume urine	Kind of urine	Treated with H₂SO₄	Time of aeration. Hours	Volume 0.1 N NaOH. Cc	Calc. as benzoic acid per 1,000,000.
A	100	Fresh	+	36	0 14	17 08
A	200	Fresh	+	17	0 25	15 25
B	100	Fresh	(a)	9	0 14	17 08
B	200	Fresh	(b)	6	0 25	15 25
C	2000	Fresh	+	16	0 40	2 44
D	1500	Fresh	+	16	0 20	1 63
E	2000	Fermented	+	45	0 00	0 00

(a) Sample (B) was collected in dilute sulfuric acid and was permitted to stand for 2 mos., then 10 cc of 20% sulfuric acid was added to the 100 cc

(b) Here 20 cc of 20% sulfuric acid was added

Since benzoic acid was found in normal urine in the largest quantities of any acid, it is here taken as the basis of calculations. Of course, when urines are treated with sulfuric acid and are then aspirated or distilled, hydrochloric acid is volatilized, hence the above concentrations, as indicating organic volatile acidity, are too large. These experiments, however, show that: (1) the normal acidity of urines is not largely due to volatile acids; (2) the odor of urines at ordinary temperature cannot be caused by numerous aromatic acids, at least, it cannot be caused by such acids present in any considerable quantity.

In fact, the extremely low concentration of volatile acidity may be caused almost entirely by hydrogen sulfide; this will be shown in the following experiments:

The Occurrence of Hydrogen Sulfide in Urine.

It was observed that all urines treated with dilute sulfuric acid slowly evolved hydrogen sulfide. It became necessary to determine. (1) whether such hydrogen sulfide was formed from the added sulfuric acid; (2) whether the presence of acids accelerated the evolution of hydrogen sulfide; and (3) whether other odors were developed at the same time. Samples of urine were treated in the following indicated manner:

Fraction of same sample	Volume used Cc	Treated with	Effects on lead acetate paper after			
			3 hrs	4 hrs	48 hrs	11 days
A	100	4 g H₃PO₄	edges blackened	darker	very dark	black
B	100	4 g H₂SO₄	edges blackened	darker	very dark	black
C	100	.				edges blackened

Here it is concluded: (1) the hydrogen sulfide was not formed by reduction of the sulfuric acid; (2) its evolution was accelerated by acids, and (3) the untreated sample gave off little or no hydrogen sulfide. The further observation was made that both (A) and (B) but not (C) gave off urinod-like odors.

From these and other observations the conclusion is drawn that treat-

ment of urines with sulfuric acids yields hydrogen sulfide, urinod, a dark brown precipitate and other reaction products.

Methods Used for the Isolation of Volatile Substances.

Two methods have been employed by us to obtain volatile substances in urine:

1. Direct extraction of urines with ether.
2. Extraction of distillates of urine with ether.

Since large quantities of urine and ether were handled in both cases, considerable thought and labor were given to the best methods of experimentation. Three methods were pursued:

Method I.—Three carboys each holding about 40 liters were arranged at different levels (see Fig. 1), so that the contents of the topmost one (A) siphoned into the middle one (B) and the latter into the lowest one (C).
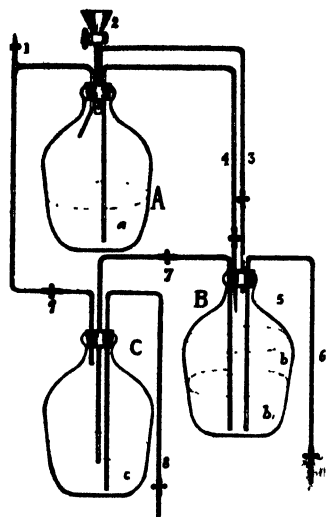
Fig. 1.

The purposes of this apparatus were these: (1) to extract large quantities of urine or its distillates *automatically* by making use of gravity; (2) to avoid loss of ether attending the handling in open vessels; and (3) to avoid danger of fire in working with large quantities of ether.

A sufficient quantity of ether (*b*) is drawn into (B) through (6), by closing (3), (4) and (8) and drawing through detached (9). With screw-clamp (1) opened, bottles of urine or distillate are inverted in funnel (2) and are permitted to empty into carboy (A). When the latter is nearly full, screw clamps (3), (6) and (8) are closed and urine or distillate is siphoned to (4) by drawing at detached (9). A steady stream of urine or distillate spurts through the finely drawn nozzle (5) and, with proper adjustment, break to a fine spray when striking the surface of the ether. With (9) reattached, (3) opened and (1), (6) and (8) and stopcock (2) closed, carboy (A) will empty into (B) and if siphon (7) is filled by drawing at (7) carboy (B) may simultaneously deliver into (C). Hence, without any attention or danger of loss, the apparatus may be set in operation during the day and be permitted to run all night. Since sediment from (A) may clog the nozzle (5), the siphon of (A) should not dip too deeply, nor should this siphon be opened before the sediments have had time to settle. Of course, when such clogging results, tube (5) may be detached and cleaned.

When the ether layer (*b*) becomes much reduced, it may be drawn off

and fresh ether may be added, or better, more and more ether may be added when necessary, without removing any of the layer present.

The extracted liquor from (B) and (C) may be drawn off at (6) and (8), most advantageously when (A) is refilling at (2). This lower aqueous layer contains large quantities of dissolved ether, hence should be distilled to recover the same. This may conveniently be effected by running the liquor directly into the vessel used as a still or the liquor may be preserved for distillation in bottles. The distillation was most conveniently carried on with a battery of flasks such as used for Kjeldahl digestions. The tubes from the different condensers were connected so that one tube only delivered into the receiver and this was surrounded by flowing tap-water and carried a return condenser. The ether distillates containing water were assembled and returned to carboy (B).

Method II.—This, like Method I, is safe and ether-saving. It is semiautomatic, prevents disagreeable odors being liberated in the laboratory but is not so rapid as Method III.

The apparatus (see Fig. 2) consists of bottles (A) delivering urine by siphons (1) through jets (5) into the large bottle (B), which carries two return condensers, one of which (E) opens to the air by a capillary tube (3) at the top to accommodate changes of pressure in (B). The urine having passed through the ether layer (*b*) is siphoned into flask (C); here the dissolved ether is distilled back into the extraction bottle (B). The waste material is then withdrawn through siphon (8). After a number of extractions, the ether (*b*) is siphoned from (B) to (D) where it is concentrated, the ether returning to (B) through the condenser (F).

Fig 2.

All siphons are filled by drawing with the suction pump and are controlled by screw clamps. The effectiveness of the extraction depends upon the size and force of the stream striking the ether layer.

Method III.—This method, though most wasteful of ether, was found to be rapid and convenient. The distillates from the urine were placed in ordinary 2.5 liter acid bottles, whose stoppers and necks had carefully been freed from paraffin. The bottles ordinarily were filled about four-

fifths with distillates and nearly to the neck with ether. The bottles, tightly cork stoppered, were shaken vigorously from time to time and finally were set aside, or were permitted to stand until the mixture settled in sharply defined layers. These layers were separated by one of three methods: (1) one or two bottles were emptied into a large separating funnel and the two layers were drawn off in the usual manner; (2) a siphon was used to draw off the aqueous layer from each bottle; (3) the contents of many bottles were poured into a carboy and the two settled layers were separated by the siphon.
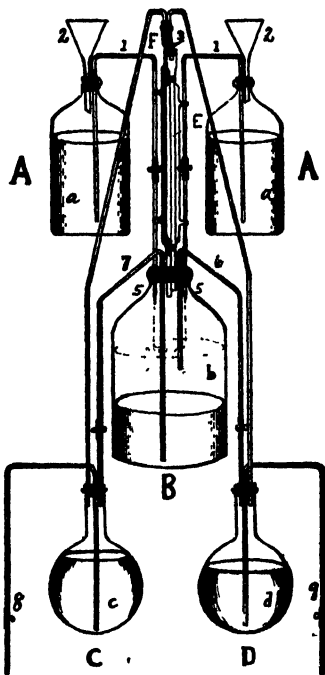
The aqueous part was distilled to recover dissolved ether and this ether was used for the other extractions. In all cases the hot residual aqueous solutions gave off uriniferous odors, showing that the extraction of volatile substances was not complete with a single extraction.

Collection and Chemical Treatment of the Urine.

The collection of urine was managed so that it was treated either directly with sulfuric acid, or within a few hours, thus avoiding fermentation.[1] Concentrated sulfuric acid was diluted with one volume of water, and 100 cc. of this solution were placed in each 2.5 liter acid bottle   Then funnels were placed in the necks of the bottles for direct collection or the bottles were filled from large flasks or bottles containing fresh urine. Thus the urines were treated almost immediately with 3-4% of sulfuric acid, enough to unite with all of the reactive constituents of urine, and to yield a definite though weak hydrolyzing medium.

The bottles thus filled were set aside, preferably in a warm, dark, place for a number of days. During this time the color of the solution becomes chocolate-brown or brown-black, a brown precipitate is formed, and characteristic uriniferous odors are developed. If moist lead acetate paper is held in the vapors of these bottles, blackening results, showing invariably the presence of hydrogen sulfide.[2]

Since urines extracted directly gave only small quantities of volatile substances, it was found that some hydrolytic treatment, as with sulfuric acid, was not only productive of but necessary for the evolution of the desired volatile substances.

Three lines of study were followed—the urines were:

(1) Extracted directly with ether.
(2) Digested with dilute sulfuric acid and then were subjected to distillation—practically to dryness.
(3) Permitted to ferment and then were subjected to distillation.

The first method was nearly unproductive of volatile substances—showing that these are largely formed by fermentation, hydrolysis, etc., from

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[1] Fermented urines give little urinod and much indol in the "neutral" portion.

[2] See following contribution for further evidence that hydrogen sulfide is found in all urines.

conjugated compounds. The treatment with dilute sulfuric acid, distillation, and extraction with ether was found to be a very satisfactory method for the isolation of volatile substances of urine. The third method was unsatisfactory for the production of volatile substances of urine.

The Distillation of Urines.

The urine, treated with sulfuric acid and permitted to stand many days, was decanted into round-bottomed flasks connected by Hopkins' bulbs to ordinary condensers. These flasks rested on tripods covered with sand baths, wire gauzes, or wire gauzes supplied with circular-hole asbestos shields.

With fermented urines, foaming-over, necessitating redistillation, was a source of much trouble, until the volume was reduced to about one-third. Such difficulty was not met with in case of acid-treated urines. Since the distillation was continued practically to dryness, trouble from bumping was experienced after some two-thirds of the volume was obtained as distillate. When the bumping stage was reached, the concentrated urines were cooled, assembled and permitted to stand so as to precipitate the sediments which were usually dark brown in color. The urine was then siphoned off and the distillation was continued. This process was repeated until the urines were so concentrated that they solidified almost completely on standing. The liquid part of this, however, was filtered off and distilled further.

The first distillate contained traces of floating oil, which tended to cling to the wall of the receivers. It possessed the characteristic urine odor and exercised nauseating and depressing effects upon the worker. The middle fractions seemed to yield less oil and possessed a modified odor suggestive somewhat of creosote. The final fractions contained some light yellow solid[1] and possessed a putrid odor mixed with the odor of sulfur dioxide. Throughout the distillation the odors, at different times, resembled urine, old peanuts and most varieties of intestinal gas.

Treatment of the Ether Extracts.

After concentrating by distilling, the ether solutions were repeatedly and successively treated with aqueous solutions of (A) sodium carbonate, (B) sodium hydroxide, and (C) hydrochloric acid. The residual ether solution was distilled first directly to remove the excess of ether and finally with steam to separate (D), the very volatile, from (E), the less volatile neutral substances. In this manner were obtained fractions containing: (A) volatile acids, (B) volatile phenols, (C) volatile bases, (D) urinod, etc., (E) urinod hydrosulfide, etc.

To illustrate the complexity and variety of the volatile substances of urine, the boiling points of these fractions are given:

[1] See page 2134.

(A) up to 260° mostly at 220–260°.
(B) up to 320° mostly at 170–200°.
(C) up to 100°.
(D) up to 170° at 29 mm. mostly at 108° 29 mm.
(E) above 170° at 29 mm.

(A) The Volatile Acids of Urine.

From 125 liters of urine, the aqueous solution in sodium carbonate (A) gave with an excess of dilute hydrochloric acid:

(a) A copious precipitate of white crystals (mostly benzoic acid).

(b) An aqueous acid-containing solution.

(a) *The Solid Insoluble Volatile Acids.*—After filtering and drying 9.8 g. of crystals were obtained or one part in 12,700 parts of urine. This solid contained at least three substances, viz., benzoic acid, a *putrid acid*, and dark odorous substances insoluble in ammonia. The melting point of the mixture was 117° (benzoic acid, 121°).

(b) *Soluble Volatile Acids.*—These were separated from the aqueous solution by extraction with ether. After evaporating the ether, an oily residue was obtained, it was dissolved in an excess of dilute alkali and then filtered through paper moistened with water. The alkali solution was treated with hydrochloric acid and extracted with ether. The ether solution was dried with fused calcium chloride and distilled. The following fractions were taken:

(a) From 125 liters			(b) From the last third[1] of 1000 liters		
Fraction	B p	Weight	Fraction	B p	Weight
(1)	50°	0 02	(1)	90°	0 50
(2)	50–80°	0 50	(2)	90–120°	0 62
(3)	80–120°	· 0 50	(3)	120–220°	3 62
(4)	120–220°	?	(4)	220–245°	7 84
(5)	220–255°	?	(5).	245°	3 24
(6)	255–270°	(m p 47°)			
(7)	270°		Total		15 82

Fractions 1 and 2 gave, with ammoniacal silver nitrate, a black precipitate of silver indicating formic acid.[2] All the fractions with neutral ferric chloride gave reddening and precipitates of basic ferric salts, thus indicating the presence of fatty acids or merely weak volatile acids. Fractions below 120° gave, with alcohol and hydrogen chloride, a heavy oil but no perceptible odor of ethyl acetate. Fractions above 220° solidified to white, soapy crystals of a peculiar fetid odor. These were identified as largely benzoic acid, as containing members of the fatty series of acids and possibly as containing hexahydrobenzoic or some closely related acid.

Some of the fractions boiling above 220° were dissolved in ammonia,

[1] Unfortunately, the acids from the first two-thirds of the distillate from the 1000 liters were lost

[2] Strisower, *Biochem Z* , 54, 189; *C A* , 8, 174.

filtered and boiled with an excess of silver nitrate and the precipitated silver salts were extracted with successive portions of hot water; thus there were obtained, on cooling, the following fractions:

	I.	II	III	IV
Weights taken	0 1144	0 1355	0 1048	0 4069
Found, Ag	45 63	46 86	47 04	46 94

Calculated for C_6H_5COOAg, 47 12; $C_6H_{11}COOAg$, 45 91; $C_6H_{13}COOAg$, 45 52

These data indicate that: (1) the original mixture of solid acids consists of benzoic acid largely; (2) the other acid or acids have greater molecular complexity than benzoic acid.

From some of the 7.84 g. of solid acids obtained from the 1000 liters of urine, silver salts were prepared in different fractions and thoroughly washed with water. After decomposing the respective fractions with an excess of hydrochloric acid, the acids were extracted with ether and then were isolated in the usual manner.

Fractions	Crystals	M p	Remarks
(1)	Transparent flakes	124°	Melted sharply
(2)	Transparent flakes	106°	Remelted at 119°, optically inactive
(3)	Compact crystalline mass	105°	Sublimed to plates and needles
(4)	Compact crystalline mass .	122°	
(5)	Compact crystalline mass	121°	Sublimate melted at 122°

Since none of these fractions gave precipitates with bromine water, they contained no salicylic or other hydroxy acids. These experiments confirmed the conclusion that the solid volatile acids of urine consist largely of benzoic acid. The putrid-smelling, low-melting acid was suspected to be hexahydrobenzoic acid.[1]

Some of the fraction boiling between 220–250° and freed from benzoic acid as much as possible by crystallizing from hot water, was extracted with ether, brought into water and treated with an excess of silver oxide. The hot aqueous solution was filtered and the first crop of crystals was discarded, for silver benzoate is less soluble than silver hexahydrobenzoate.[2] The second crop separated as white flakes.

0 1732 and 0.1103 g gave 0.0794 and 0 0508 g. Ag; Calc. for $C_6H_{11}COOAg$ Ag. 45.91%, Calc. for C_6H_5COOAg· Ag, 47 12%; found· 45.84 and 46 05%

[1] This acid was first prepared by Aschan and is described as forming colorless leaflets melting at 30° and boiling at 232–233°. It is sparingly soluble in cold water and readily soluble in hot water. It is more easily volatile with steam than benzoic acid and possesses an odor resembling valeric acid and ethyl crotonic acid   Aschan, *Ber*, **24**, 1864, 2617; **25**, 886; *Ann.*, **271**, 261; Markownikoff, *Ber*, **25**, 370, 3357; Haworth and Perkin, *J Chem Soc*, **65**, 103; Bucherer, *Ber.*, **27**, 1231, Einhorn and Meyenberg, *Ber.*, **27**, 2829; Einhorn and Lumsden, *Ann*, **286**, 264, Sabatier and Murat, *Compt rend.*, **154**, 922; Godchot, *Bull. soc chim*, **9**, 261

[2] Bucherer, *Ber.*, **27**, 1231.

Some of the silver salt was heated in a sealed tube with an excess of ethyl bromide; the ethyl ester[1] boiled up to 195°.

Though apparently the presence of hexahydrobenzoic is indicated the evidence is not conclusive. For instance, when the free acid was separated from the silver salt, it did not solidify at ordinary temperatures. It contained no sulfur and no nitrogen. It responded to the ferric chloride test. It did not react with a chloroform solution of bromine. It did not react with a sodium carbonate solution of potassium permanganate. Small, white needles of its lead salt, melting at 40°, contained 42.34% Pb; lead benzoate melts at 114° and contains 46.10% Pb, lead hexahydrobenzoate contains 44.89% Pb, lead heptylate contains 44.49% Pb, lead caprylate melts at 84° and contains 41.98% Pb.

The fraction boiling at 120–220° (last third of 1000 liters) was refractionated and converted into silver salts.

| | | Silver salts contained % Ag | |
Fraction	Boiling	First crop	Last crop
(1)	120–160°	51 94	56 45
(2)	160–190°	51 70	51 67
(3)	160–220°	47 00	46 46

Calc for $C_4H_{13}COOAg$ Ag, 45 52%, C_5H_9COOAg Ag, 48 38%; C_6H_9COOAg Ag, 51 63%, C_6H_7COOAg Ag, 55 34%

These boiling points and analyses indicate the presence of butyric acid in (1), the presence of valeric acid in (2), and the presence of caproic and heptylic acids, and possibly hexahydrobenzoic acid in (3).

The above experiments show that the volatile acids of urine consist mostly of benzoic acid and fatty acids up to and including caproic acid, probably heptylic and possibly hexahydrobenzoic or some closely related acid.

From 200 liters of fermented urine, 0.53 g. of volatile acids were separated. Since most of this solidified to needles of benzoic acid, it is seen that fermentation is nonproductive of volatile acids of urine.

Since benzoic acid is the most voluminous volatile acid of hydrolyzed urine but is not detected in normally acidic urines subjected to direct extraction with ether, it is concluded that all the benzoic acid of urine is conjugated as hippuric acid.·

(B) *Volatile Phenols of Urine.*

The aqueous alkaline solution (see above) was acidified with hydrochloric acid and extracted with ether, After drying with anhydrous sodium sulfate, it was fractionated as follows:

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[1] Aschan gives 195° as the boiling point of ethyl hexahydrobenzoate, *Ann.*, **271**, 264

		I. 125 liters (H₂SO₄).	II. 1000 liters (H₂SO₄).			III. 200 liters (fermented).
			(a) first ½;	(b) last ½;	(c) total.	
(1)....	170°	0 00	1.00	0 34	1 34	0 02
(2)....	170–200°	0.95	17 32	1 81	19 13	4.23
(3)...	200–230°	0 39	6 38	1 74	8 12	0 58
(4)	230–260°	0 20	0 20	0 47	0 67	0 33
(5)	260–320°	0 80	1 29	1 16	2 45	1 00
		2 34	26 19	5 52	31 71	6 16

It will be observed that *phenols occur about 31 parts in a million of urine.* All the lower distillates gave turbidity with bromine water, thus indicating the presence of phenols. Some tarry residue remained in the distilling flasks, this indicating decomposed higher phenols. The third fraction, when treated with an excess of bromine and boiled, gave an oil which solidified on cooling. When treated with alcohol, golden flakes, softening at 264° and melting at 280°, were obtained. It has not been identified. It and the other phenolic compounds will be studied further.

(C) Volatile Bases of Urine.

Only a little basic volatile substance is given off when urines are distilled with sulfuric acid. Of course, this is formed by the hydrolysis of sulfates. Since the distillates of such urines are acid, the bases remain in the ether-extracted, aqueous portion as salts of hydrochloric acid, etc. No effort was made to recover such bases from distillates after extracting with ether. However, in the preparation of neutral fractions of the volatile substances of urine, the ether solution was always washed with dilute hydrochloric acid to remove bases possibly present.

(a) An effort was made to obtain volatile bases from urine. Forty liters of urine, collected over sufficient potassium hydroxide to maintain a strong alkaline reaction, was extracted twice with ether after the phosphates had been removed. The ether from both the extracted material and the aqueous portion was distilled over dilute hydrochloric acid to collect low-boiling bases. Evaporation of this aqueous solution gave 2.38 g. of hydrochloride. After extracting the residue with absolute alcohol, an insoluble portion was obtained. It formed a platinum salt containing 43.15% Pt; calculated for $(NH_4)_2PtCl_6$, 43.96% Pt. The portion soluble in absolute alcohol (0.091 g.) yielded a platinum salt containing 41.17% Pt; calculated for $(CH_3NH_3)_2PtCl_6$, 41.32% Pt. This experiment shows that *methylamine is present in alkali-treated unfermented urine only about one part in a million of urine.*

(b) Fourteen liters of urine were allowed to ferment one month. After freeing from earthy phosphates, it was extracted twice with ether. The ether was distilled into receivers containing hydrochloric acid; some ammonium carbonate and rectangular crystals of a musty odor formed in the condenser. From 3.259 g. of the hydrochlorides, 0.108 g. of alcohol-

soluble crystals were obtained. Its platinum salt contained 41.26% Pt; calculated for $(CH_2NH_3)_2PtCl_6$, 41.32% Pt. This experiment shows that *methylamine is present in alkali-treated fermented urine one part in 100,000 or ten times as much as in case of the unfermented urine*.

(*c*) From 200 liters of fermented urine, 0.15 g. of bases was obtained; here no effort was made to obtain low-boiling bases. The residue solidified largely on cooling and possessed the odor of indol.

(*d*) From 1000 liters of acid-treated urine 0.5 g. of bases was obtained.

(D) *Volatile Neutral Substances of Urine.*

The ether solution from the original distillates of urine, after concentrating and treating with acids and alkalies, was further concentrated and distilled with steam. In this manner easily volatile substances were removed from difficultly volatile substances contained in the original distillate and from paraffin and other impurities introduced during the course of the experiments.

The steam distillation gave at least five different substances, *viz.*, sulfur and urinod hydrosulfide in the residual liquor, and a low-boiling thiocompound, urinod, and a high boiling compound in the steam distillate. The latter distillate also contained some sulfur. The presence of sulfur was observed at various stages of the distillation of the urine. It collected as a light yellow solid in the distillate and the condenser, especially during the final distillations. It melted at 114.5–115° and by the Carius method gave 100% S. Since sulfur itself is not volatile with steam, its formation must result from decomposition of hydrogen sulfide or from some other sulfur-containing compound. Since acids were removed by previous treatment with alkalies, hydrogen sulfide[1] cannot be present as such in the neutral fraction; hence it must be formed by decomposition of some neutral complex substance.

The residue from the steam-distillation was light brown in color, was easily soluble in alcohol but difficultly soluble in water. When warmed with acids it slowly gave off the odor of urinod and hydrogen sulfide. It was obtained in larger quantity from 40 liters by direct extraction than from 1000 liters by distillation. If it is *urinod hydrogen sulfide*, this latter result is to be expected. Since it has not been freed from impurities its further investigation will be postponed. Should it prove to be urinod hydrogen sulfide it will account not only for the sulfur and hydrogen sulfide obtained but also for the conjugated form of urinod.

After the neutral fractions were distilled with steam, they were extracted with ether. This ether solution was dried with calcium chloride and shaken in a separating funnel with metallic mercury to remove sulfur. The ether solution was concentrated and finally distilled *in vacuo*.

The first distillate up to about 100° at 30 mm. always contained oil,

[1] See "The Occurrence of Hydrogen Sulfide," p. 2125.

with an allyl mustard oil or ethyl xanthate odor. Since about 0.5 g. of it has been obtained it will be further investigated. The middle fraction contained the urinod, which will be described in the following paper. The final fraction contained an oil boiling at 170° with 29 mm. pressure. The final fraction did not react with semicarbazide.

The yield of neutral substances from urine directly extracted with ether was practically nil. The yield from fermented urines was 2.44 g. from 200 liters; about equal quantities of urinod and indol were obtained. The yield from sulfuric acid-treated urines was 9 g. from 1000 liters.

(E) Residues from Urine.

When urines were distilled with dilute sulfuric acid in the manner described above, two residues were obtained: (1) a chocolate-brown precipitate was formed when the urines were concentrated and (2) a salt-like residue was formed when the urines were evaporated to dryness.

The first,[1] containing chromophoric substances, is a mixture of acids, such as uric, benzoic, etc., for it is completely soluble in alkalies and is reprecipitated by acids. After long standing at ordinary temperatures, an enveloping sublimate of pure crystals of benzoic acid was observed.

The brown portion of the mixture has not been investigated. Apparently its formation is contemporaneous with the formation of urinod. If the latter proves not to be combined with hydrogen sulfide in fresh urine, it may possibly be combined with the chromophoric substance.

The second residue, obtained by evaporating urines and consisting largely of sodium sulfate, was redissolved in water, treated with dilute sulfuric acid and extracted four times with ether. After concentrating the ether solution, needle-like crystals, melting at 183° and identified as hippuric acid, were obtained. Since no other substance could be obtained from the ether, it is concluded that ether extracts from urine only volatile substances and hippuric acid.

Summary.

(1) A review of hitherto known volatile substances of urine shows that they are not responsible for its characteristic odor. Some of these, as ammonia, indol and possibly the phenols, contribute to the composite nature of the odor

(2) Fresh and fermented urines possess lower vapor pressures than water.

(3) At ordinary temperatures the volatile acidity of urine is very minute.

(4) Direct extraction of urine with ether yields only a little volatile substance.

(5) Distillation of urines with dilute sulfuric acid yields the largest

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[1] Edlefsen, *Munch med Wochsch*, **45,** 1615, 2524, mentions a precipitate of creatinine when urines are treated with sulfuric acid　See also THIS JOURNAL, **36,** 415 (1914).

quantities of volatile substances. These distillates were extracted with ether, concentrated and distilled.

(6) The volatile substances were separated into four major fractions: (*a*) acids, (*b*) phenols, (*c*) bases, and (*d*) neutral substances.

(7) The four fractions distil over a wide range of temperatures, hence, they are, respectively, mixtures of many substances.

(8) The principal volatile acid was found to be benzoic acid (formed by hydrolysis of hippuric acid); hydrogen sulfide, the fatty acids up to heptylic acid, and possibly hexahydrabenzoic acid.

(9) The principal phenols are phenol and *p*-cresol; other higher phenols occur in notable quantities.

(10) Methylamine and indol occur as a trace in fresh urines and in larger quantities in fermented urines.

(11) The neutral substances of urine are the most important contributors to the odor of urine. Urinod and at least three other new substances were indicated.

SEATTLE, WASH.

URINOD, THE CAUSE OF THE CHARACTERISTIC ODOR OF URINE.

BY WILLIAM M DEHN AND FRANK A. HARTMAN.

Though many references are made in the literature and text-books[1] to the characteristic odor of normal urine, the direct association of this odor with chemical compounds is loosely made only to ammonia and to several volatile acids.[2] The odor of fresh urine is described as not unpleasant, while the offensive odor of fermented urine is described as ammoniacal. Apparently, the substance that imparts to all urines the characteristic odor has been overlooked by previous investigators. This substance we have isolated and analyzed; its formula is C_6H_8O and we have given to it the name *urinod*.[3]

[1] Black, "The Urine in Health and Disease," 1896, p. 25: "In the normal condition fresh urine has a peculiar aromatic odor The smell of urine is said to be due to the presence of phenylic, taurylic and demoluric acids....when it has undergone decomposition in the bladder it exhales an ammoniacal odor and sometimes gives off sulfuretted hydrogen;" Menninger, "Diagnosis of the Urine," 1900, p. 17: "The odor is sharp and slightly aromatic, and its cause is at present unknown;" Long, "Urine Analysis," 1900, p. 13: "The odor of urine is not easily described, as in health it is *sui generis* and characteristic;" Holland, "The Urine," 1904, p. 18: "Putrid urine has the odor of ammonia modified;" Tyson, "Practical Examination of Urine," 1903, p. 33: "The characteristic odor of urine....is putrescent and ammoniacal, the former (resulting) from decomposition of mucus."

[2] Salkowski, *Z. physiol. Chem.*, 13, 264 (1889).

[3] Latin, *urina*, urine; *odor*, smell.

If a quantity of urine is treated with sulfuric acid in the proportions of 100 to 3 and the mixture is permitted to stand for some days and is then distilled, oily films may be seen on the surfaces of the distillates and, after using the same receivers for many distillates, the inner surfaces may be seen to be coated more or less with oil   This oil is largely urinod   In this form, its odor, though very disagreeable and characteristic of urinod, is mixed with other odor imparting substances   To obtain it pure in quantities sufficient for analysis, many liters are necessary, 1000 liters were distilled and 700 liters of distillate were taken—this ultimately yielded 5 18 g of nearly pure urinod   Of course, some was lost during the handling, acidulation, distillation, ether extraction, concentration, treatment with acids and alkalies, distillation with steam, reextraction, drying, and distillation *in vacuo*   From data at hand, it is estimated that *urinod occurs to the extent of only 1 2 parts in 100,000 parts of urine*   For the reason that its occurrence in urine is so small, its presence has not previously been recognized   At least, no method for its separation has previously been worked out   Even now, after three years of systematic search and laborious experiments, its separation is effected only with great difficulties

Preparation of Urinod.

As was described in detail in the previous paper, the separation of the neutral volatile substances containing urinod consisted of the following outlined operations   The urine was treated with dilute sulfuric acid so as to make about 3% concentration of acid   The mixture was permitted to stand a number of days   The urine, now darkly colored and giving off unpleasant odors, was distilled and the distillates were extracted with ether   After washing with aqueous solutions of sodium carbonate, sodium hydroxide and hydrochloric acid to remove acids, phenols and bases, the ether solution, containing neutral substances, was concentrated to a small volume and then was subjected to steam distillation   The distillate was extracted with ether and the ether solution was shaken with metallic mercury, to remove sulfur, etc   The ether solution, always yellow or brown at this stage, was dried and further concentrated and fractionated *in vacuo*

From 1000 liters of urine the following pure[1] fractions were obtained

[1] In an earlier experiment, not making use of all the refinements of the above method 125 liters of urine were distilled and fractions were taken as follows (A) the first 50 liters, (B) the second 50 liters and (C) the remaining distillate   The ether extracts from these distillates were concentrated and treated with anhydrous potassium carbonate which of course removed acids but not phenols   To (C) was added the tarry residues from the distillations (A) and (B), the ether solution of (C) was then treated with sodium carbonate to remove acids, and with potassium hydroxide to re-

From the first 700 liters of distillate.				From the remainder of the distillate.		
	Grams	*t*	*p*		Grams	*t*	*p*
(1)	1 31	108°	30–29 mm	(1)	1 1867	100°	31 mm
(2)	2 21	108–113°	29 mm	(2)	0 5181	100–120°	31 mm
(3)	1 66	113–128°	29 mm	(3)	0 9575	120–140°	30 mm
	—			(4)	0 2767	140–160°	29 mm
Total	5 18			(5)	1 0216	160–175°	29 mm
				Total	3 9606		

Fraction 2 was used most largely for analysis, though Fraction 3 gave quite concordant data.

Calculated for C_6H_8O C, 75 01, H, 8 33, O, 16 66
Found   C, 75 08, H, 8 19, O, 16 73
Found   C, 75 01, H, 8 08, O, 16 91
Found   C, 74 95, H, 8 26, O, 16 79
                    Average, C, 75 01, H, 8 18, O, 16 81

Calculated molecular weight   96 06
(With McCoy's apparatus, boiling point method)
Found (with ether as the solvent)   94 90   95 20
Found (with benzene as the solvent)   97 90

Since the most refined methods failed to show the presence of other elements, the empirical formula is established as C_6H_8O

The boiling point of urinod is 108° at 28 mm.   Its boiling point is estimated to be about 208° at ordinary pressure; however, it cannot be dis-

move phenols   After drying with calcium chloride, the ether solution was concentrated and distilled *in vacuo*

Distillate	Fraction	Weight	Temperature	Pressure	Color
A	1	0 1767	105–108°	32–26	Brown to red
	2	0 6097	110–110 5°	25–24	Yellow
B	1	0 1208	111°	28	
	2	0 4594	102–108°	28	
C	1	?	106–118°	32–31	
	2	?	124–130°	30	
	3	0 2489	148–174°	30	
	4	0 6205	179–210°	30	
Total		2 2356			

Here phenols, sulfur and probably paraffin contaminated the urinod   Analyses of these impure fractions, especially of A–2, showed approach to the percentages of composition of urinod

Calculated for C_6H_8O C, 75 01, H, 8 33, O, 16 66
Found   C, 69 25, 72 40, 71 30, 69 19, 71 81, 69 13
Found   ,   H, 8 33, 8 06, 8 01, 8 01, 8 07, 8 27
Found   N,   7 15, 13 06 18 00
Found   S,   1 61 (333° in Carius tube)

The nitrogen indicated was found to be largely carbon monoxide—urinod decomposing with almost explosive violence   The trace of sulfur was probably owing to free sulfur. Some of these fractions yielded free iodine when treated with nitric acid, this was probably distilled from iodides contained in the urine

tilled at ordinary pressure without decomposition. Urinod does not solidify in an ordinary freezing mixture. It is a light yellow oil, slightly heavier than water. It is soluble in ordinary organic solvents, but is insoluble in water. It is very volatile with steam. It has a very penetrating, persistent, nauseating odor of urine. A drop of urinod placed upon filter paper retained its odor after fifteen months. It is very toxic, as will be shown in a following paper.

Urinod darkens rapidly in direct sunlight, reduces potassium permanganate and ammoniacal silver nitrate in the cold, reacts with Millon's reagent, but not with Fehling's reagent or an alkaline solution of picric acid. With fixed alkalies the odor of urinod is changed to a terpene-like odor.

Derivatives of Urinod.

Nitro Derivatives.—Urinod reacts with concentrated nitric acid with explosive violence, with dilute nitric acid its disagreeable odor is quickly destroyed. Apparatus containing traces of urinod may be freed from the same by mere washing with nitric acid.

For the preparation of nitro derivatives, cold, dilute nitric acid is added to the urinod and the mixture is permitted to stand for a day. Needles or brown sticky masses are obtained. After drying on a clay plate and recrystallization from hot water, golden needles melting at 78° were obtained.

Calc for $C_6H_6N_2O_5$· C, 38 71, H, 3 22, found C, 39 01, H, 3 90

The *dinitro urinod* is easily soluble in ether, benzene and chloroform, less soluble in water and carbon disulfide. When first formed it was probably mixed with an oily *mononitro urinod.*

With Semicarbazide.—A mixture of equimolecular quantities of urinod, semicarbazide hydrochloride, and sodium acetate in a water-alcohol solution was heated for several hours under a return condenser. Gradually, a granular precipitate formed. From 1 1 g. of urinod (Fractions 1–3), 0 4 g. of the precipitate was obtained. The crystals were insoluble in all organic solvents, practically insoluble in water, but soluble in alkali, from which hydrochloric acid slowly precipitated thin, hexagonal leaflets melting at 254°. The hot alkali solution gave off ammonia, indicating decomposition.

	Calculated for		Found.		
	$C_4H_{11}O_2N_6$	$C_4H_{12}O_2N_6$.	I	II.	III
C	25 11	24 84	24 67	24 50	24 07
H	5 79	6.77	5 97	5 64	6 43
O	25 12	24 87			
N	43 98	43 52	45 69	46 10	.

Too little evidence is at hand to judge of the nature of this compound

except that: (1) it represents a split portion of urinod;[1] (2) it is a *complex acidic compound.*

With Hydroxylamine.—When an equimolecular mixture of urinod, hydroxylamine hydrochloride, and sodium acetate in alcohol-water solution, was permitted to stand, or was heated to 100° in a sealed tube, only an oil of a modified not unpleasant odor, which did not solidify in a freezing mixture, was obtained

With Bromine.—When urinod was treated either with bromine water or with bromine contained in carbon tetrachloride, hydrobromic acid and a dark colored sticky mass were obtained   This mass was nearly odorless and consisted of at least two compounds (1) a solid soluble in chloroform and ether but insoluble in absolute alcohol and melting at about 110°, (2) a solid soluble in chloroform, insoluble in ether and not melting at 250°   Owing to the small quantities on hand these bromo derivatives were not studied further

The remarkable chemical properties of urinod are shown not only in the vigor of reaction with various reagents but also in their almost universal formation of secondary reaction products   For instance, with bromine, two or more substances are obtained, with hydroxylamine, no crystallizable oxime,[2] with phenylhydrazine, no crystallizable hydrazone, with semicarbazide, an anomalous compound, with nitric acid, an oil and a small yield of the dinitro derivative, all these chemical properties argue for an exceptional formula for urinod

The Constitution of Urinod.

The formulas[3] agreeing with the properties of urinod thus far studied are as follows

(a)   (b)
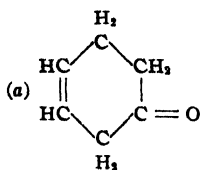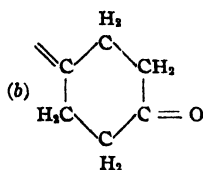
(3 Cyclohexane ion)   ("Tetrahydro semiquinone")

[1] Since Fraction 4 of the urinod distillates did not yield this compound but all the lower fractions did, it is evident that the crystalline compound is a product of urinod

[2] For peculiar reaction of 2 cyclohexene 1 on with hydroxylamine see Kötz and Grethe, *J prakt Chem* 80, 473   They obtained an oxime melting at 75–76° and 3 hydrooxyaminocyclohexanonoxime melting at 49–51°   For oxidizing influences of hydroxylamine, see *J prakt Chem* [2] 29, 497 *Ber* 19, 305, 20, 614 29, 2080

[3] Pentamethylene keten is also a possible formula

$$CH_2—CH_2$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2—C=CO$$
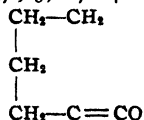
(1) Urinod is insoluble in hot dilute solutions of hydrochloric and sulfuric acids, hence it cannot contain a basic (or alcohol-oxygen or ether-oxygen) group.

(2) Urinod is insoluble in dilute solutions of alkalies, hence it cannot contain an acidic or phenolic group

(3) Urinod is optically inactive, hence, if not a racemic mixture, it cannot contain an asymmetrical carbon atom

(4) Urinod reacts with bromine contained in carbon tetrabromide, giving a strong evolution of hydrogen bromide and a solid bromo derivative, hence it is a *cyclic* compound

(5) Urinod reacts with cold, dilute nitric acid, giving golden needles of *dinitro-urinod*, melting at $78°$ and possessing the formula $C_6H_6N_2O_5$, hence it is a *cyclic* compound

(6) Urinod reacts with *semicarbazide* Forming a compound melting at $254°$, hence it is a *ketone* or an *aldehyde*

(7) Urinod reacts with hydroxylamine, phenylhydrazine and hydrogen sulfide, forming derivatives not possessing the characteristic odor of urinod These compounds, though not purified and analyzed, indicate the presence of the *carbonyl* group in urinod

(8) Urinod is easily oxidized by ammoniacal silver nitrate, also by aqueous solutions of potassium permanganate, thus indicating close relation with hydrobenzene derivatives

Known compounds possessing the same empirical formula as urinod but not agreeing with it in properties are the ethyl and dimethyl furanes,[1] acetyldimethylacetylene[2] and the following

(c)
```
CH = C—CH₃
|
H₂C
|
CH₂—C = O
```

(d)
```
CH₂—CH
|
C—CHO
||
CH₂—CH
```

(e)
```
        CH
H₂C    ╱    ╲CH
|              |
H₂C    ╲    ╱C = O
        C
        H₂
```
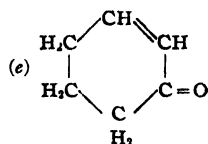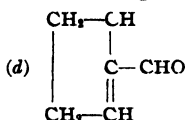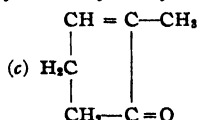
(2 Methyl 2 cyclopentene 1 on)[3] (1 Cyclopentene 1 aldehyde)[4] (2 Cyclohexene 1 on)

2-Cyclohexene-1-on,[5] with which urinod is assumed to be isomeric, also the homologs of the former, differ widely from urinod in properties

[1] Priebs, *Ber*, **18**, 1362 Dietrich and Paal *Ber* **20**, 1085 Fisher and Lavcock, *Ber*, **22**, 103, Laycock *Chem News* **78**, 224 Nasini and Carrara *Gazz chim ital* **24**, 278

[2] Griner *Ann chim phys* [6] **26**, 369 This compound boils at 149–150° and possesses the formula CH₃COCH₂ C C CH₃

[3] Looft *Ann* **275**, 372 *Ber* **27**, 1538 Bouveault *Compt rend* **125**, 1184 This compound boils at 157° and possesses a sharp aromatic odor

[4] Kekulé, *Ann* **162**, 105 Baeyer and H v Leibig *Ber* **31**, 2107 This compound boils at 172° possesses the odor of benzaldehyde and is quite soluble in water Its semicarbazone melts at 208°

[5] Kotz and Götz *Ann* **358**, 183 Kötz and Grethe *J prakt Chem*, **80**, 473, Kotz, Blendermann, Mahnert and Rosenbusch **400**, 72, Tshugaer, *J prakt Chem*, **81**, 188.

	B. p.	M. p. semicarbazone
(a) 3-Cyclohexene-1-on (urinod).	108° at 29 mm.	254°
(e) 2-Cyclohexene-1-on..	63° at 14 mm.	161°
3-Methyl-2-cyclohexene-1-on	81–85° at 13 mm	
3,6-Dimethyl-2-cyclohexene-1-on	75° at 19 mm	
2,3-Dimethyl-2-cyclohexene-1-on	119° at 12 mm	225°

The 2-cyclohexene-1-on possesses many properties of a phenol, indeed it is supposed to possess the tautomeric from of 1,5-dihydrophenol;[1] this, like phenol, tetrahydrophenol,[2] and hexahydrophenol,[3] but unlike urinod, is soluble in water as well as in alkalies. Thus, since all these compounds, as well as the dihydrophenols, are eliminated from the discussion of the constitution of urinod, only formulas (a) and (b) remain.

From considerations of the cresols, the diphenols, the monohalogen phenols, the monohydroxy anisols and phenetols, etc., it is observed that the boiling points of the meta and para compounds are some 10–40° higher than the corresponding ortho compounds. By analogy, it may be assumed that a compound with the formula (a), with its double bond more distant from the oxygen atom than a compound possessing the formula (e), would have a higher boiling point. This may be especially true of a compound of the formula (b), and thus the high boiling point of urinod may be accounted for.

Some of the terpene ketones may be considered to be homologues of urinod. For instance, (f) dihydrocarvone[4] is 2-methyl-5-isopropyl-urinod, while (g) terpenone,[5] (h) carvenone[6] and (i) 3-terpene-5-on[7] are methyl-isopropyl homologues of Kötz's 2-cyclohexene-1-on.

```
                CH =.CH                          CH₂—CH
                |    |                           |    ||
(f)  C₃H₇CH  HC CH₃            (g)  C₃H₇CH    C.CH₃
                |    |                           |    |
                CH₃—CO                           CH₂—CO

                CH₃—CH₂                          CH₃—CH
                |    |                           |    ||
(h)  C₃H₇C   HC.CH₃            (i)  CH₃.CH    C.C₃H₇
                ||   |                           |    |
                CH —CO                           CH₂—CO
```

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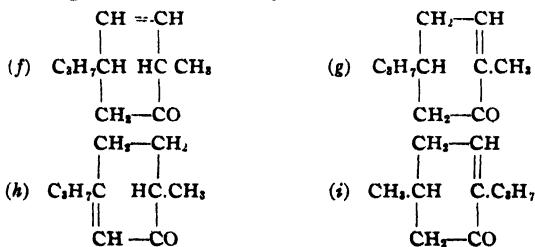
[1] Kötz, etc., *Ann*, **400**, 72   The 3,6-dimethyl-2-cyclohexene-1-on is described as possessing a pleasant menthone-like odor.

[2] Baeyer, *Ann*, **278**, 97. This compound boils at 166° and is quite soluble in water.

[3] Baeyer, *Ann*, **278**, 97; Markownikow, *Ibid*, **302**, 20   This compound boils at 161° and is soluble in 28 volumes of water

[4] Wallach, *Ann*, **275**, 115; **279**, 378; **300**, 290, 313, 368, **314**, 164; Brühl, *Ber.*, **32**, 1225.

[5] Baeyer, *Ber.*, **29**, 35

[6] Wallach, *Ann.*, **277**, 122; **286**, 130, **287**, 381; **305**, 270, Baeyer, *Ber.*, **27**, 1921; **28**, 1592; Tiemann and Semmler, *Ber.*, **31**, 2889

[7] Wallach, *Ann*, **305**, 272; Baeyer, *Ber*, **28**, 1587; Kremers, *Am Chem J.*, **16**, 395; **18**, 762.

A comparison of boiling points:

(a)	3-Cyclohexene-1-on (urinod)	108° at 28 mm	.
(b)	2-Cyclohexene-1-on	63° at 14 mm	
(f)	Dihydrocarvone	104° at 18 mm	222° at 760 mm
(g)	Terpenone		235° at 760 mm
(h)	Carvenone	112° at 14 mm	236° at 747 mm
(i)	3-Terpene-5-on	97° at 12 mm	208° at 760 mm

shows that some of the homologs of (e) are higher boiling than dihydrocarvone, the homologue of urinod. Of course, the establishment of the constitution of some of these formulas is doubtful, so that conclusions drawn therefrom as to the relative boiling points of (a) and (e) cannot be final.

That urinod may possess the exceptional formulas (b) gathers support from consideration of its characteristic toxic properties and its odor— the isocyanides and other bivalent[1] carbon compounds being both toxic and malodorous

It is of special interest to study the properties of urinod in connection with other closely related compounds, such as quinone and tetrahydrobenzaldehyde.

(1) Urinod, quinone, dihydrocarvone, and 3-tetrahydrobenzaldehyde[2] all possess similar solubilities, strong odors and closely related structural formulas, compare (a) and (f) with the following:
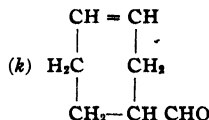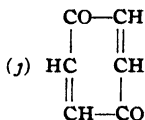
(2) Urinod and quinone are both yellow in color and darken on standing in sunlight.

(3) Both urinod and 3-tetrahydro-benzaldehyde polymerize readily.

(4) Urinod, dihydocarvone and tetrahydro-benzaldehyde are extremely easily oxidized—a general property of reduced benzene compounds.

Urinod Occurs in the Conjugated Form.

That urinod does not occur free in fresh, normal urine is concluded from consideration of the following evidence

(1) The odor of freshly voided urine is not pleasant, i. e., in such urine the odor of urinod itself is absent, or is present only as a trace, that is its conjugated form is not unpleasantly evident to the sense of smell.

(2) Fermentation, or treatment with hydrolyzing agents, develops

[1] See the views of Nef, *Ann*, **280**, 303, **287**, 274, **298**, 202, also see Wade, *J Chem Soc*, **81**, 1596, Lawrie, *Am Chem J*, **36**, 487

[2] Sobecki, *Ber*, **43**, 1040 The odor is described as extremely unpleasant, suggestive of benzaldehyde and isovaleric aldehyde Compare with hexahydrobenzaldehyde, Frezouls, *Compt rend*, **154**, 707

very unpleasant odors, which, though composite, as will be shown, are easily recognized as containing urinod.

(3) Urinod itself is very toxic, as will be shown, hence for physiological reasons, it must be transformed to the innocuous, conjugated form to be eliminated.

(4) Urinod is easily volatile with steam, but each fraction of distillate from urine and even the heated residue gives off the odor of urinod, hence not only is its formation by hydrolysis difficult, but, *a priori*, it must exist in the conjugated form.

(5) This conclusion gains further support from consideration of many of the other substances in urine, which are shown to be in the conjugated form. For instance, ammonia is conjugated in urea; urea, in uric acid and other purine bases; benzoic and phenylacetic acid, in hippuric and phenylaceturic acids; phenol, p-cresol, other phenols, indol, skatol, etc., in sulfonates and glycuronates.[1]

The Odor of Urine.

The odor of urine, though largely caused by urinod, is blended with basic, acidic, phenolic and other neutral compounds, under different conditions of alkalinity, acidity and neutrality. Since urinod is not found in fresh urine in the free state, its offensive odor is not developed unless urine is permitted to ferment, is evaporated or ignited, is treated with acids or alkalies, or is secreted under pathological conditions.

The odors of fresh urines, evaporating urines, fermenting urines, distillates from alkali-treated urines, distillates from acid-treated urines and even different fractions of the latter two, all possess the characteristic odor of urinod but are quite readily distinguished by the sense of smell, for the reason that secondary odoriferous substances also are present.

Fresh urine possesses only a slight odor, which probably is caused by the conjugated form of urinod or by its partial splitting into urinod.

Urines, while being evaporated and ignited, probably possess the odors of urinod, conjugated urinod, indol, the lower fatty acids, phenols and other undetermined substances.

Fermenting urines probably possess the odors of urinod, ammonia, ammonium sulfide, indol and phenols.

Urines treated with alkalies probably possess the odors of ammonia, alkylamines, indol, phenols and urinod.

Urines treated with acids, as was shown in the previous paper, possess the odors of a great variety of volatile substances, but especially the odors of urinod, the lower fatty acids and the simple phenols.

Since urea and other urinary compounds occur in small quantities in

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[1] For comprehensive experiments on alicyclic compounds in combination with glycuronic acid in urine, see Hämäläinen, *Skand. arch. Physiol.*, **27**, 141; see also Levy, *Biochem Z*, **2**, 314 on the conjugation of glycuronic acid with optical antipodes.

perspiration, and since in cases of obstructed excretion of urine they occur in larger quantities in perspiration, it may be concluded that the conjugated form of urinod or urinod itself may also be excreted by the skin. That such is the case is quite evident to one familiar with the odor of pure urinod. Indeed this body odor may also be a large factor in the composite odor of ill-ventilated, occupied rooms.

The Use of Antiseptics in Urinals.

The various preparations for urinals can have only three uses:

(1) Destructive effects upon bacteria.

(2) Destructive effects upon uriniferous odors.

(3) Solvent effects upon earthy phosphates, etc.

As was shown in a previous paper,[1] most preservatives for urine have only partial inhibitory power, unless applied in quite concentrated solutions. It is doubtful whether the quality or the quantity of the antiseptics ordinarily applied in urinals have any meritorious bactericidal effects.

The most important odor-imparting substances of urine are ammonia, phenols, aliphatic acids, indol and urinod. Since all these substances, except urinod and indol, are soluble in water, intermittent flushing of urinals with water will remove all but traces of urinod and indol.

Since urinod, the most ill-smelling substance of urine, is easily acted upon by free halogen to form inodorous derivatives, the use of bleaching powder in urinals has scientific basis. The use of naphthalene, other hydrocarbons, and phenols, with which urinod is not chemically reactive, can have no justification beyond their feeble antiseptic effects. These and many other commercial preparations may mask but not destroy the odor of urinod.

Oxidizing reagents, such as bleaching powder, the halogens, nitric acid, the oxides of nitrogen, permanganate solutions, etc., speedily destroy urinod. Of course, bleaching powder, the halogens and the higher oxides of nitrogen themselves possess disagreeable odors and, therefore, are objectionable reagents for urinals.

Because of its insolubility in water and ordinary cleansing materials, urinod is removed with difficulty from the hands of the worker in the laboratory. This property of urinod accounts for the failure to remove odor of urine from lavatories by ordinary methods of cleansing.

Strunk[2] made extensive investigations of oils for urinals and concluded that they consist chiefly of creosote oils and petroleum. Such oils, having weak disinfecting power, act chiefly as deodorizers and cleansing agents. They cannot, however, have chemical effects upon urinod and their solvent effects upon it hardly justifies their use.

[1] THIS JOURNAL, 36, 409 (1914).

[2] Veröff, Geb. Militär-sanitatswes., 45; Arch. hyg., Chem. Untersuchungsstellen, IV, 31 (1911); Apoth. Ztg , 26, 146, 156, 167; C. A , 5, 2681.

It is concluded from our studies that frequent use of water for flushing purposes in urinals and the occasional application of dilute nitric acid as a washing material is effective not only for destroying the urinod but also for dissolving earthy phosphates and other precipitated materials.

The Physiological Significance of Urinod.

For the reason that urinod is found at day or night in all normal or pathological urines, like urea, uric acid, creatinine, etc., it must bear some constant relation to metabolism. From evidence at hand, the relation of urinod to the body functions remains purely speculative or unknown.

It is our purpose to make a systematic search for the tissues originating urinod and to determine whether it is an absorption product of intestinal putrefaction or it is a waste product of metabolism. These and further studies of the chemical properties of urinod are reserved.

Summary.

(1) A neutral ill-smelling substance, with empirical formula, C_6H_8O, has been separated from urine. Its structural formula probably is 3-cyclohexene-1-on. It occurs in urine in the conjugated form and is set free by fermentation and the decomposing effect of dilute sulfuric acid.

(2) It is a most characteristically smelling compound and seems to be excreted in all samples of urine.

(3) Its relation to metabolism, though apparently constant, is at present unknown.

(4) It is very toxic and may bear some relation to uremia.

SEATTLE, WASH

SOME OBSERVATIONS ON THE EXCRETION OF CREATININE BY WOMEN.

BY MARY HULL.
Received July 7, 1914

The following observations are submitted as a contribution to the question of the extent of creatinine elimination under varying conditions. The relations in general have been studied by several writers, especially by Folin[1] and by van Hoogenhuyze and Verploegh,[2] while the points to be covered here are concerned with only one phase of the subject, *viz.*, the extent of creatinine excretion in a group of women in normal health with a normal diet. The long papers of van Hoogenhuyze and Verploegh contain a mass of data throwing light on the relation of the excretion to certain diets, and also the course of the excretion in pathological conditions, especially in high fevers. But the subjects of the observations were men, in the normal cases, at least, and the question of the relations

[1] Folin, Hammersten's *Festschrift* and other contributions, largely *Journal of Biological Chemistry*.

[2] van Hoogenhuyze and Verploegh, *Z. Physiol. Chem.*, **46**, 415 (1905), **57**, 161 (1908).

in women is not touched upon. The daily output of creatinine is closely related to body weight, but more especially to the weight of the muscular portion of the body and its activities.

In the course of some other studies in this laboratory an opportunity was presented to make some observations on the excretion of women and the results of these observations are here given. While the creatinine output was the most important factor considered, the nitrogen excretion in other directions was also considered. The subjects of the studies were a group of women nurses in the Wesley Memorial Hospital, associated with Northwestern University Medical School. The women were all in normal health and consumed a moderate diet, the extent of the protein content of which is suggested by the figures given below. The height and weights of the women are given in this table.

TABLE I.

No	Height	Weight
1	5 ft 0 in.	47 1 kg
2	5 " 9 "	77 0 "
3	5 " 5 "	62 5 "
4	5 " 5 5 "	62 1 "
5	5 " 7.7 "	65 7 "
6	5 " 3 "	47 7 "

No. 1 appeared small and plump; No. 2, tall and heavy, without appearing fat. No. 3, who weighed less than 2, gave the impression of fat rather than muscle weight. No. 4, with nearly the same height and weight as 3, appeared relatively slight. No. 5 was tall and spare, while No. 6 appeared small, thin and wiry.

The urine samples were collected in 24-hour portions from 7 A.M. to 7 A.M. and preserved by toluene. The volume, reaction and specific gravity were observed on each day's excretion. The ammonia and creatinine nitrogen fractions were determined each day, and composites, for analysis, were made of the excretions for 6 days. For each subject four such composites were made, that is, each woman was under observation through one month, with the exceptions noted. The nitrogen determinations were made by the usual standard methods, and in particular the urea nitrogen by the Benedict method and the creatinine nitrogen by the Folin method by the aid of a Duboscq colorimeter.

The numerical results obtained are shown in Table II.

In general the values for the nitrogen distribution show nothing unusual except in the relation of the creatinine to the ammonia nitrogen. The latter runs about as might be expected but is, in the mean, higher than the creatinine in percentage distribution because this seems to be somewhat low. The creatinine relations are best shown in Table III where the average values for each woman for the whole period are given:

TABLE II.—ANALYSES OF COMPOSITES

Sub No	Date 1913	Vol C.c.	Sp gr	Total N	Urea N, g	Urea N, %	Am N, g	Am N, %	Creat N, g	Creat N, %	Uric acid N, g	Uric acid N, %	Undet N, g	Undet N, %
1	VI, 30–VII, 5	1035	1 014	5 24	4 23	80 70	0 441	8 40	0 259	4 90	0 063	1 20	0 25	4 77
	VII, 14–VII, 19	912	1 016	4 90	3 90	79 78	0 482	9 80	0 262	5 40	0 073	1 49	0 18	3 67
2	VI, 30–VII 5	533	1 029	8 01	5 56	81 80	0 474	5 90	0 342	4 50	0 144	1 80	0 49	6 12
	VII, 7–VII, 12	855	1 021	7 14	5 85	81 90	0 532	7 40	0 338	4 70	0 123	1 72	0 30	4 20
	VII, 14–VII, 19	870	1 021	7 56	6 20	82 00	0 458	6 10	0 341	4 50	0 105	1 38	0 46	6 08
	VII, 21–VII, 26	985	1 017	6 14	4 80	78 20	0 463	7 50	0 300	4 80	0 039	0 63	0 54	8 79
3	VI, 30–VII, 5	421	1 031	6 71	5 33	79 50	0 517	7 70	0 276	4 10	0 051	0 76	0 54	8 04
	VII, 7–VII, 12	997	1 020	8 78	7 64	87 10	0 425	4 80	0 313	3 60	0 126	1 44	0 28	3 19
	VII, 14–VII, 19	553	1 028	7 60	6 37	83 82	0 464	6 11	0 282	3 70	0 118	1 55	0 37	4 87
	VII, 21–VII, 26	647	1 023	6 38	5 14	80 50	0 420	6 58	0 273	4 30	0 112	1 76	0 44	6 90
4	VI, 30–VII 5	395	1 030	6 66	5 81	87 30	0 267	4 00	0 279	4 20	0 084	1 26	0 22	3 33
	VII, 7–VII 12	725	1 023	8 14	7 22	88 70	0 377	4 30	0 323	3 90	0 130	1 60	0 09	1 11
	VII, 14–VII, 16	740	1 019	9 24	8 14	88 09	0 371	4 02	0 295	3 20				
	VII, 21–VII, 26	943	1 024						0 319					
5	VI, 30–VII, 5	772	1 026	7 96	6 58	82 70	0 478	6 00	0 313	3 90	0 149	1 87	0 44	5 52
	VII, 7–VII 12	1103	1 016	7 29	6 00	82 30	0 469	6 40	0 289	4 00	0 114	1 56	0 52	7 13
	VII, 14–VII, 19	1160	1 017	7 98	6 72	84 20	0 530	6 60	0 318	4 00	0 139	1 74	0 27	3 38
	VII, 21–VII, 26	1260	1 017	9 56	7 90	82 64	0 534	5 59	0 293	3 10	0 142	1 49	0 69	7 22
6	VI, 30–VII, 5	950	1 018	6 92	5 93	85 60	0 420	6 10	0 240	3 40	0 072	1 04	0 28	4 05
	VII, 7–VII, 12	1600	1 010	6 83	5 61	82 10	0 389	5 70	0 262	3 80	0 108	1 58	0 47	6 88
	VII, 14–VII, 19	1065	1 013	6 39	5 42	84 76	0 380	5 94	0 254	3 97	0 113	1 83	0 22	3 44
	VII, 21–VII, 26	1005	1 015	7 30	6 10	83 60	0 364	4 99	0 247	3 40	0 117	1 60	0 47	6 44

TABLE III.

Subject No.	Weight Kilos	Creatinine Grams per day	Creatinine Mg per kilo
1 .	47 1	0 705	14 97
2	77 0	0 886	11 51
3	62 5	0 768	12 28
4	62 1	0 816	13 12
5	65 7	0 820	12 48
6	47 7	0 674	13 92

It will be seen at a glance that these amounts of creatinine, in terms of milligrams per kilogram of body weight, are lower than are usually reported, and much lower than the average for men.   In the lengthy observations cited by Hoogenhuyze and Verploegh the creatinine excretion varied between about 27 and 31.5 milligrams per kilo of body weight daily, in the earlier series of experiments, and between 22 7 and 26.6 milligrams in the later series.

In several extended series of investigations carried out in this laboratory by Professor J. H. Long, on male medical students under definitely controlled conditions of diet, the daily excretion was found to be much higher.   In one of these series[1] the means for six men, 120 determinations in each case were,

TABLE IV

Wts of subjects Kilos	Creatinine excretion Mg per kilo, daily
82 7	21 56
69 4	24 61
58 2	27 83
60 6	24 95
69 9	26 28
69 5	25 27

In other series of observations, not yet published, the creatinine values are somewhat lower, but very much higher than found in the case of the women

It must be recognized that in the employment of the subjects we may find a partial explanation of the apparent anomaly.   As nurses, their work was wholly indoors with exercise and other muscular exertion deficient. While the highest gross weight of creatinine excreted is found in Subject No. 2, whose body weight is the highest the milligram per kilo excretion is the lowest.   The heavy body weight is not due to apparent fat, but to bone and muscle, with the former evidently in excess.   In the cases of the other women there is no apparent relation between body structure and creatine excretion.

While this work was in progress another case presented itself in the person of a corpulent woman employed in the same hospital as helper in the pantry.   Her work was wholly indoors and not such as to occasion

[1] See Long and Gephart, This Journal, 34, 1229 (1912)

much exertion. Her diet was ample, but the water consumption was very low. For some fancied reason as to ill effects on digestion this woman drank beer more commonly than water. Her urine was collected and analyzed on six consecutive days, with the following data:

TABLE V

Body weight	95 6 kilos	
Height	5 ft 5 in	
Mean urine vol	567 cc	
Specific gravity .	1 029	
Total N g	9 38	
Urea N, g	7 53	
Ammonia N, g	0 473	
Creatinine N, g	0 246	Creatinine = 0 661
Uric acid N, g	0 132	
Creatinine, mg per kilo	6 91	

Perhaps no great importance can be attached to this very low value because the woman's condition was in a sense abnormal, and especially in the lack of proper physical exercise. But in the following figures we have the results of the analyses of the urine of three women who lived at home and whose daily life embraced a normal routine of work and rest, with a moderate normal mixed diet. The results given are the means for the excretion of six consecutive days.

TABLE VI

Subject	A		B		C	
Weight	62 1 kg		53 5 kg		74 3 kg	
Vol urine	953 cc		1283 cc		662 cc	
Sp gr	1 024		1 015		1 028	
Total N	8 20 g		7 20 g		7 25 g	
Urea N	6 82	83 2%	6 03	83 7%	5 91	81 4%
Am N	0 312	3 8	0 319	4 5	0 426	5 5
Creat N	0 282	3 5	0 265	3 7	0 289	4 0
Ur acid N	0 169	1 9	0 154	2 2	0 118	1 6
Rest N	0 63	7 6	0 430	5 9	0 510	6 7
	....		. . ..		.	
Creatinine .	0 759		0 712		0 772	
Mg per kilo	12 22		13 31		10 46	

Here, as in the other cases, we find a low creatinine excretion, when expressed in terms of body weight. Subjects A and B were women of moderate weight and structure, C with a height of 5 feet 5 inches, was relatively fat. The low urine volume is to be noted in this case. To check increasing weight the subject has lived on a somewhat restricted diet for years.

Taking all the figures into consideration, it is evident that the subjects studied exhibit a low creatinine excretion in comparison with the usual values as found for men. To determine whether this is true in general with women would call for long observations on other groups. These observations are offered as suggestive of an interesting question. There

is no peculiarity in the distribution of other nitrogen factors and no reason is apparent why there should be.   In the case of the creatinine we have the fact of lower muscular structure and lower muscular tone to possibly account for the observed findings.

This series of observations was made at the suggestion of Prof. J. H. Long in the summer of 1913.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL
CHICAGO, ILL

A COMPARISON OF METHODS FOR THE DETERMINATION OF THE PROTEOLYTIC ACTIVITY OF PANCREAS PREPARATIONS.

BY J H LONG AND A W BARTON
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In recent years many suggestions have been made as to methods for finding the tryptic power of various pancreas preparations, but these still leave the problem of a generally definite method far from solution

For a long time the classic Kuehne method was held in esteem as a standard for the comparison of other procedures and it still has its uses Often egg albumin has been employed instead, but its digestion, as compared with the fibrin of the Kuehne scheme, is so slow that practically it is much less suitable as a substratum.   The mistake of employing raw egg has often been made, although it is known that trypsin has but little action on other than denatured proteins   It was recently pointed out by one of us[1] that many of the results reported by Wroblewski, Bednarski and Wojczynski[2] are rendered meaningless by this use of raw egg in the estimation of tryptic activity.   In some cases this resistance to digestion seems to be due to the presence of the so-called antitrypsin in the native protein solution.   That this is the case with serum has been shown by several authors, for example by Oppenheimer and Aron,[3] but the structure of the native protein itself is a strong factor, and possibly the strongest one, in the case of raw egg   In any event uncooked egg can not be well used to show tryptic activity.

While shreds of fibrin are well adapted for the purpose of a qualitative test of the proteolytic power of pancreas extracts, there are many difficulties in the way of successful use in quantitative comparisons.   Some of these difficulties are inherent in the use of a solid substance which can not be acted on uniformly by the digesting medium.   The rapidity of digestion will depend on the degree of comminution of the fibrin and on the frequency of shaking the test vessels.

An equally important objection to fibrin is usually overlooked and it is not clearly stated in the literature.   It is this, that even after the most

[1] Long and Johnson, THIS JOURNAL, 35, 1194 (1913)

[2] Beitr chem Physiol und Path , 1, 288 (1902)

[3] Ibid , 4, 279 (1904).

careful purification fibrin retains the peculiar ferment which brings about, more or less rapidly, the phenomenon described as fibrinolysis, resulting in the gradual solution of the fibrin. This fact, long known, does not appear to have been sufficiently considered where fibrin has been used. Fibrin kept in glycerol, as often recommended, changes in a few days at the ordinary temperature; indeed, a weight of a hundred grams or more in glycerol may become quite liquid in ten days or two weeks. Even where the water is removed as far as possible by glycerol and the chopped mass is pressed dry and treated with toluene, autolysis still takes place in time, as pointed out by one of us[1] before. For satisfactory quantitative comparisons it is essential that the fibrin be practically fresh.

The uncertainty in the employment of solid substance is avoided by the use of normal milk, as originally suggested by Roberts[2] in his studies on pancreatic ferments. The Roberts method is based on the observation of the so-called metacasein reaction. Ordinary milk does not coagulate on boiling, but if its casein be modified in a certain way, coagulation on boiling follows readily. The modified product was called metacasein by Roberts and is similar to the caseogen of Arthus and Pagès, and the paracasein of other authors, in the first stages of their production. In a given small quantity of milk the coagulation on boiling is not observed until the whole of the casein has been converted to this stage. The value of the test depends on this point. By longer digestion the reaction disappears, because the casein is converted further into true derivatives. The unit of measurement in the test is the number of milligrams of milk converted to give the metacasein reaction in five minutes by 1 milligram of the ferment.

It will be recognized at once that there are certain weighty objections to this as a quantitative test. Roberts seemed to regard the composition of market milk as sufficiently uniform for the purpose, but this can not be the case. The casein content of milk is, of course, variable where the product of individual cows is considered, but the value for mixed market milk has been assumed to be pretty constant, with the casein about 3%. We are inclined to think that the average casein content of the mixed milk delivered in our cities is lower than it was some years ago. Under city ordinances relating to milk the fat is made the most important constituent and in consequence cows are selected and fed for fat production. In our experiments the average casein content of the milk used was about 2.5% and a change in this would naturally make a change in the amount of ferment required to complete the test. This will be discussed below.

Retaining a casein solution as the substratum for digestion, and aiming

[1] Long and Johnson, *loc. cit.*
[2] Sir William Roberts, M.D., F.R.S., *Proc. Roy. Soc. (London)*, **32**, 145 (1881).

at greater precision to be secured by employing a definite substance, Gross[1] recommended a weak solution of sodium caseinate. Small constant volumes of such a solution are mixed with gradually diminishing volumes of the dilute tryptic solution and incubated an hour at 38° (or 40°). At the end of the time the test tubes containing the mixtures are removed from the bath and treated with 3 drops of a very weak acid solution, which produces a precipitate in the tubes in which the digestion has not reached the proper stage. As the reaction is sharp it is possible to recognize at once the tube in which the digestion just fails to be complete. A convenient number of steps in the dilutions must be chosen to give close results. The object of the test is to determine how many cubic centimeters of the casein solution may be digested by 1 cc. of the ferment solution in the unit of time, here 1 hour. A better measure, when dealing with solid ferments, is to find the number of milligrams of casein changed by 1 mg. of the ferment to the point where no precipitate is formed, in the unit of time. The tryptic activity varies inversely as the weight of ferment required and the time.

In place of making the dilutions with water, which has a destructive action on the strongest ferments free from excess of salts, we have experimented with the use of a phosphate mixture to preserve a constant low hydroxyl content but little above neutrality, as will be explained below.

In addition to these three general schemes we have carried out, with the six ferments employed, a series of tests with the formaldehyde titration as worked out by Sörensen and colleagues. Here again we employed casein dissolved in the right amount of sodium hydroxide as the substratum and after digestion through definite periods titrated, after the addition of the formaldehyde, to measure the amino acids formed. For the purposes of quantitative comparisons we have not thought it desirable to follow out the optical method, in which the measure of digestion is preferably the change in rotation in some artificial polypeptide, or certain other methods in which the liberation of tyrosine from one of its simple polypeptides is the measure of the digestive activity. For the practical purpose in view, the methods referred to give the most direct and easily followed results.

Trypsin is employed at the present time not only in the course of scientific research but also as an agent of protein digestion on the large scale, and as a remedy in the experimental study of disease, or in the routine treatment of various disorders. It is produced as a commercial product by many firms and some of the products obtained are stronger than any which the ordinary laboratory worker is likely to be able to prepare himself. Some standards for the valuation or comparison of these "trypsins"

[1] *Arch. exp. Path. und Pharm.*, **58**, 57 (1906). This work is based on the method of pepsin digestion suggested by Fuld, where edestin was used as the substratum.

or "pancreatins" is desirable, as each manufacturer makes his own state-
ment of value in terms which are sometimes vague and not translatable
into other terms.

In the investigations of the Council on Pharmacy and Chemistry of
the American Medical Association the question of the comparison of these
standards has come up more than once and the present study is the result
of an effort to throw some light on these points.[1] The plan of our study
has been this: We have made tests with six well-known American com-
mercial brands of trypsins, representing strong as well as relatively weak
preparations, and have compared their activity by the four methods
outlined above. The important details of the tests will now be given.

The Roberts Metacasein Reaction.

It is not a difficult matter to secure uniform and consistent re-
sults by this test, which is carried out practically as follows: 50
cc. of fresh milk are diluted to 100 cc. with water, the ferment
solution to be added later making part of the final volume. A num-
ber of flasks are prepared with the milk and the right amount of
water added. The smaller ferment volumes are placed in test tubes,
and flasks and tubes are warmed to 40° in a thermostat. When the
temperatures are constant the contents of the tubes are poured into the
proper flasks and the liquids mixed by shaking. At the end of each minute
a 5 cc. portion is withdrawn from each flask and quickly boiled. If
a coagulation occurs at the end of four to six minutes with one of the
dilutions, the result with this flask is regarded as a close approximation
to the proper value and a second test is made with dilutions which should
give the end point in an interval very near to 5 minutes. Roberts showed
that for time intervals nearly the same the inverse relation between time
and strength holds, as in many similar reactions. In other words, if it
is found that 5.1 mg. of the ferment is sufficient to bring about the reaction
in 4.5 minutes, 4.41 mg. will do it in 5 minutes. The dilution to 100 cc.
was always observed.

Milk from several dairies were used in the course of the investigation
and in different trials the casein content was found to be about 2.5%
by the Van Slyke-Bosworth titration. The following figures show some
typical results obtained on different days with milk from one dealer:

Four samples of milk of 50 cc. each gave 2.5, 2.5, 2.4, 2.6% casein and 4.1, 4.1,
3.9, 4.2 mg. of ferment, respectively.

In the mean, a trifle over 4 mg. of the active ferment was required to bring
about the reaction. The results are not always as close as the above

and it is almost always necessary to have two persons to make the tests so as to make the boilings at the right instant of time.

In a preliminary series of tests with a product which we will call Trypsin A, made up to a dilution of 2 mg. to 1 cc., we found these results, which are illustrative of many others:

Mg of ferment added:	6 o	5 o	4 2	4 1	4 o	
Time of onset of reaction (min.).	3	4	4 5	5 o	5 5	
Mg. for 5 minutes calculated:	3.6	4.0	3.8	4 1	4 4	Mean, 4 o

In general, values like the first are rejected and new tests made. A large number of tests were made with this same trypsin on milks obtained on different days from the same dairy. From 3.8 to 4.1 mg. of the ferment were required to produce the metacasein reaction in 5 minutes, the mean value being 4.0 mg. This will be used in the comparisons below. It was found that with other milks more of the ferment was required as the content of casein ran up to about 2.8%. This is a point which every one working with the test will have to observe.

As a further illustration of the degree of uniformity which may be expected in the working of the test the following series is given, a product which we mark Trypsin B being used. Two dilutions were employed, in one 200 mg. to 100 cc. and in the second, 600 mg. to 100 cc. The following table shows the results of the trials:

Mg of ferment added	12	12	15	15 8	15 8	16	16	17
Time to onset of react. (min.)	6 o	6 25	4 75	5 o	5 o	4 5	4 5	4 o
Mg for 5 minutes, calc.	14 4	15 o	14 3	15 8	15 8	14 4	14 4	13 6

Mean, 14 7

It will not be necessary to give the details of the other experiments as they showed about the same variations as above. By repeating them and taking mean values the results given below were obtained. The means for all of the samples are here tabulated:

Name of sample·	Trypsin A,	B,	C_I,	C_{II};	Pancreatin D,	E,	F
Mg. for 5 minutes calc..	4 o	14 7	27 3	24 3	32 9	33 8	47 3

Trypsins C_I and C_{II} were different preparations from the same manufacturer of which C_{II} was the fresher. In the comparisons below, it alone will be used. In this preparation dilutions of 700 mg. to 100 cc. were made, while with numbers D, E and F the favorable dilutions were found to be 0.870, 1.5 and 1.7 g. in 100 cc., respectively. These dilutions were not found at once but only after a number of trials with different strengths and with different samples of milk. It will be seen that the weakest product has less than one-tenth the strength of the strongest.

_ The values given present a fair picture of the behavior of the better grades of such preparations available in this country. All these samples have some amylolytic as well as proteolytic activity but are practically devoid of action on fats. A considerable number of other preparations

examined were found to be weaker than these, but need not be discussed here because no new principle is involved in the experience gained with them.

The probable reason for the variations in the individual series is found in the character of the products used. These are not soluble extracts but more or less insoluble powders which are brought into solution as well as possible by rubbing up in a mortar with successive portions of water. Even with this treatment we can not be certain that all of the true enzyme has left the solid and gone into solution. Heat can not be applied in the making of the solutions and they must be made fresh, as loss of strength always follows in dilute aqueous solution on standing. The variations from possible changes in casein content of the milk must not be lost sight of.

But this variation in the casein content has not the effect calculated if there is a variation in the dilution at the same time. A change in the dilution changes the concentration of the enzyme with reference to the casein, and this is an important point. Changes in the dilution give somewhat perplexing results. All the above values are based on trials with milk containing almost exactly 3% of fat as well as the uniform casein content mentioned. It has been recently shown that increase in the fat of milk increases the time required in the ordinary rennet coagulation,[1] and it is probable that the above reaction would be affected in the same way. Roberts found that the time of digestion to produce the metacasein reaction is increased greatly by dilution, and stated that if the reaction is secured with 50 cc. of milk, undiluted, in three minutes, the same milk diluted with an equal volume of water would require six minutes. In other words, the rapidity of formation of metacasein is proportional to the concentration of the ferment.

In a long series of tests we found this relation to hold only approximately, but as the point was not a necessary part of the present enquiry we have not followed it to a definite conclusion. For our purpose it was thought better to make all the comparisons under the constant dilutions, as given.

It must be kept in mind that the time given, in the practical application of the test, is the very beginning of the reaction, or onset, as Roberts called it. By long digestion the phenomenon disappears because of the formation of soluble products without the coagulating property of casein. Some little uncertainty naturally obtains in detecting just the right point of the onset of the coagulation, and this uncertainty can be overcome only by considerable practice with the method.

The following table shows the mean results of the above experiments, arranged in the order of ferment strength and with the use of the Roberts

[1] Kreidel and Lenk, *Biochem. Z.*, **63**, 151 (1914).

unit, the parts of milk converted by one part of the enzyme.   The gram
and cubic centimeter are here taken as equivalent.

Number.	A.	B.	C.	D.	E.	F.
Mg of ferment for 50 cc. of milk:	4 0	14 7	24 3	32.0	33 8	47 3
Digestion units·	12500	3400	2050	1520	1480	1060

The values in the last line will be used for the comparisons to follow.

The Sodium Caseinate Digestion, Fuld-Gross Method.

The strength of casein solution usually recommended for this method
is 1 mg. to 1 cc., that is, 0.1%. Of this solution 2 cc. or 2 mg. of casein
are to be used in each test, that is, this amount is to be added to each of
a series of test tubes along with the various dilutions of the ferment solu-
tion to be incubated for each trial.   While this weak casein solution is
satisfactory for very weak enzymes it is not as convenient for strong solu-
tions, and the practice of this laboratory has been to employ a solution
of double the strength with three times the volume, that is to use 12 mg.
of casein in 6 cc. in place of 2 mg.   The ferment is made up in solutions
of various strengths, in some cases as low as 0.05 mg. to 1 cc.

First, a series of tubes are charged with 6 cc. of the casein solution,
made as described below, and warmed to 40° in the bath.   In other tubes
the dilutions of the ferment are poured and each of these small volumes
is made up to 4 cc. and also warmed to 40°.   Then the dilutions in series
are poured into the properly labeled casein tubes, which are shaken and
digested for 1 hr. at 40°.   At the end of the time the tubes are taken from
the bath and immediately treated with 3 drops of the dilute acid, made
by mixing 1 volume of glacial acetic acid with 50 volumes of alcohol and
49 volumes of water.   Where the required digestion is complete no pre-
cipitate or cloudiness appears, but if digestion is not complete the pres-
ence of the unaltered casein is shown by the formation of a cloud, or even
a heavy precipitate.   In the records to follow, complete digestion is indi-
cated by —, and a precipitate by +, or + + if heavy.   A faint cloud indi-
cating nearly complete digestion is shown by ±.   The true end point
can be estimated by the appearance of this cloud or opalescence.

We shall not describe the experiments made with the weak solutions
referred to, but give only those where we used our stronger solution of
casein.   In some preliminary experiments we dissolved 800 mg. of an-
hydrous casein in 50 cc. of water plus 5 cc. of 0.1 N sodium hydroxide.
The solution was made to 400 cc., of which a volume of 6 cc., representing
12 mg., was taken for each test.   The ferments were made up in water
solution with 0.05 mg. to 1 cc.   The following results of Table I were ob-
tained in the trials:

TABLE I

Ferment A Cc	Ferment B Cc	Ferment C Cc	Ferment D Cc	Ferment E. Cc	Ferment F Cc
1 00++	1 00++	1 00++	1 00++	1 00++	1 00++
1 50+	1 50++	2 00++	1 50++	2 00++	2 00++
1 75±	2 00+	3 00+	2 00++	3 00++	3 00++
2 00—	2 50+	3 50±	3 00++	5 00+	4 00++
2 50—	3 00±	4 00—	4 00+	6 00±	4 50+
3 00—	3 50—		4 50±	7 00—	5 00±
			5 00±	8 00—	5 50—
			5 50—		
Activity,	Activity,	Activity,	Activity,	Activity,	Activity,
1 120–137	1 70–80	1 70	1 43–48	1 34–40	1 43–48

In another series of tests the same casein solution was used but the ferments were made up in the strength of 0.25 mg. to 1 cc. Results, Table II.

TABLE II

Ferment A Cc	Ferment B Cc	Ferment C Cc	Ferment D Cc	Ferment E. Cc	Ferment F Cc
0 10+	0 10++	0 10++	0 30++	0 30++	0 20++
0 20+	0 20++	0 20++	0 50++	0 50++	0 30++
0 25±	0 30+	0 30++	0 80++	0 80++	0 50++
0 30±	0 40+	0 40++	1 00±	1 00++	0 80+
0 35±	0 50±	0 50+	1 20±	1 50+	1 00±
0 40—	0 60—	0 60±	1 20—	2 00+	1 20—
0 50—	0 70—	0 70—		2 50—	1 50—
				3 00—	
Activity,	Activity,	Activity,	Activity,	Activity,	Activity,
1 120–140	1 80	1 80	1 40	1 · 24	1 40

These preliminary trials suggested a better system of dilution which was arranged in this way. The ferments were dissolved to make solutions of 50 mg. to 100 cc. Of these solutions, 20 cc. were, in each case, diluted to make 100 cc., giving as the final strength 0.1 mg. to 1 cc.

The casein solution was prepared by dissolving 500 mg. of pure, dry casein in 50 cc. of water plus 4.5 cc. of 0.1 N sodium hydroxide. When solution was complete about 100 cc. more of water was added and then 22.5 cc of 0.01 N hydrochloric acid to neutralize the excess of alkali and leave the casein as acid salt [1] The volume was then diluted to 250 cc, 6 cc. of this casein solution was always taken, equivalent to 12 mg.

The following series of ferment dilutions was followed and for the several ferments the parts of the series indicated were used.

No	1	2	3	4	5	6	7	8	9	10	11	12
Vol (cc).	4 0	3 6	3 2	2 8	2.4	2 0	1 6	1 2	1 0	0 8	0 6	0 4

For Ferment A, numbers 6 to 11 or 12, for B, 4 to 10, C, 1 to 8 or 9; D, 1 to 8, E, 1 to 8, F, 1 to 8 were used with a few variations, as shown The incubations were made as before.

[1] Long, THIS JOURNAL, 28, 372 (1908).

TABLE III.

Ferment A. Cc	Ferment B Cc	Ferment C. Cc.	Ferment D. Cc.	Ferment E. Cc	Ferment F. Cc
0 60+	0 80++	1 00++	1 20++	1 20++	1.20++
0 80±	1 00++	1.20++	1 60+	1 60++	1 60+
1 00—	1 20+	1 60±	2 00±	2 00+	2 00±
1 20—	1.60±	2 00—	2 40—	2 40+	2 40—
1 60—	2 00—	2 40—	2 80—	2 80±	2 80—
2 00—	2 40—	2 80—	3 20—	3 20—	3 20—
	2.80—	3.20—	3 60—	3 60—	3.60—
Actvity,	Activity,	Activity,	Activity,	Activity,	Activity,
1 · 120	1 · 80	1 75	1 60	1 .40	1 65

These results, given in Table III, are slightly different from the preliminary ones, but because of the more careful preparation of the ferment solutions, and the better dilutions, they are taken to represent pretty closely the right relations.

The ferment solutions were allowed to stand in a cool place over night, protected by toluene. The digesting values were found to be considerably diminished in five cases by the 24 hours delay and were now as follows:

A, 1 to 60;   B, 1 to 60,   C, 1 to 50,   D, 1 to 66,   E, 1 to 35;   F, 1 to 30.

The greatest change comes in the most active solution, which is an experience we have frequently observed in earlier work. With the weaker ferments the change is relatively less and in one case there even appears to be a slight gain in activity. This ferment contains the largest amount of foreign matter, especially sodium chloride and phosphate, while Ferment A is a practically soluble powder, free from tissue remains and inorganic substances.

To test the behavior of phosphate addition, and with the hope of securing a solvent which would give more uniform results than we found with water, we made up both the casein solution and the ferment dilutions in a mixture of 4 volumes of molar/100 HNa_2PO_4, and 1 volume of molar/100 H_2KPO_4, of which the hydrogen concentration is about $(H) = 0.45 \times 10^{-7}$, and the hydroxyl, therefore about $(OH) = 1.4 \times 10^{-7}$. Tests made in the same manner with this mixture, using a little more acid in the precipitation, gave the results shown in Table IV.

TABLE IV.

Ferment A Cc.	Ferment B Cc	Ferment C Cc	Ferment D Cc	Ferment E Cc	Ferment F Cc
0 40+	0.60+	0.80+	0.80+	1 20+	1.20+
0 60±	0.80±	1 00+	1.00+	1 60+	1.60+
0.80—	1.00—	1 20±	1 20±	2 00+	2.00±
1 00—	1.20—	1.40—	1 60—	2 40±	2.40—
1.20—	1.60—	1 60—	2 00—	2 80—	2.80—
				3 20—	3.20—
Activity,	Activity,	Activity,	Activity,	Activity,	Activity,
1 · 200	1 : 120	1 : 100	1 : 100	1 : 50	1 . 60

It will be seen that the phosphate stimulates the stronger and purer enzyme in marked degree but has much less action on the others. This

is probably due to the fact that some of the products, especially C, E and F, contain much tissue phosphate. These products resemble pancreas powders, rather than tryptic extracts. This behavior suggests a modification of the usual process when it comes to the examination of purified extracts of the pancreas which have been prepared in such a manner as to remove the larger part of the salts. On being allowed to stand over night, however, all the solutions were apparently weakened, but in uneven degree. This behavior would call for detailed study which can not be taken up here. For the present purpose we shall make use of the results from the water solutions only.

Digestion and Formaldehyde Titration.

The formaldehyde titration was carried out on the products obtained by the action of the ferments on relatively strong solutions of sodium caseinate, by the general process developed and improved by Sörensen and colleagues.[1] Casein solutions were made by dissolving 20 g. of dry casein in 170 cc. of 0.1 N sodium hydroxide plus 100 cc. of water. When solution was complete the volume was diluted to 500 cc. Portions of 25 cc. plus the amount of ferment to be used later were treated with 10 cc. of neutralized formaldehyde and titrated with 0.1 N sodium hydroxide and phenolphthalein, running to sharp rose red. These results were used in correction of the actual titration results later. Portions of 100 cc. of the caseinate solution were warmed to 40° in flasks. The amount of ferment to be used was rubbed up with water and the solution made to 5 cc. in each case. After warming to 40° each ferment solution was poured into a volume of the casein solution and the mixture incubated through 2 hrs. at 40°. At the end of each 30 minutes one-fourth of each volume, 26.25 cc., was withdrawn, treated with 10 cc. of the formaldehyde and phenolphthalein and titrated with the alkali. Of Ferment A 50 mg. were added to the 4 g. of casein, while of the others 200 mg. were taken. But in the tabulated results the titration values for A are multiplied by four to bring all to the same basis for comparison, as shown below. The figures are already corrected for the amount of alkali required in the blank titration, and, as given, measure the amount of amino acids liberated or developed by the digestion of 1 g. of casein contained in each 25 cc. of original solution through the added ferments.

Time. Min.	Cc. of 0.1 N NaOH required for 25 cc. of					
	A.	B.	C.	D.	E.	F.
30	32.0	10.0	13.2	12.2	11.7	10.0
60	38.8	16.2	15.8	15.1	14.7	13.2
90	45.6	17.7	17.2	17.0	16.6	14.4
120	48.8	18.7	18.8	18.7	17 7	15.9

[1] Sörensen, *Biochem. Z.*, **7**, 45 (1907); **25**, 1 (1909); Henriques, *Z. physiol. Chem.*, **60**, 1 (1909); Henriques and Sörensen, *Ibid.*, **63**, 27 (1910).

It will be seen that approximately the same order is observed here as in the casein digestion, with Ferment A much stronger than the others, and B, C and D nearly the same. In the case of A the amino acid liberation indicates a rather advanced degree of digestion. For the purpose of comparison, putting the result for A as 100, we have these values in series:

A 100,   B 38,   C 38,   D 38,   E 36,   and F 33.

For this comparison we have taken the alkali requirement at the end of the 2-hour digestion period. The relations for other times are nearly the same.

The Fibrin Digestion.

Coming finally to the oldest method for comparing tryptic values we have the following observations to record: For the reasons already suggested it is much more difficult to secure comparable results in this way than in any of the later methods suggested. As originally described, by the digestion of fibrin the simple solution was usually understood. But the first stage of this solution yields a globulin-like body which represents no very advanced condition of digestion. The choice of the right digestion period here, along with the proper weight of substance to be digested are important elements in this test. By making the period long enough even the weakest products appear to have some value and many of the results found in the literature regarding the activity of tryptic extracts are based on periods of many hours' duration or through the night in many cases. In our studies we have followed two general schemes. In the first we have started with some small, definite amount of prepared fibrin, usually 2 g., and have noted the time required to practically digest all of it. A few stray flakes are always left, even with the most active preparations. In the other case we begin with a larger weight, as 5 g., and determine the amount of soluble nitrogen formed in a definite time, as three hours or four hours. This nitrogen must be diminished by the amount obtained in a blank experiment where the same weight of fibrin is taken, with the same alkalinity of reaction, but where the ferment has been killed by heat. This plan has been varied by neutralizing the digested mixture with dilute acetic acid, boiling and filtering off the neutralization precipitate. The soluble nitrogen now found by the Kjeldahl determination on the filtrate is naturally less.

Comparing the trypsins by the first scheme we have this result. The preparations were taken in amount of 25 mg. in 50 cc. of water, plus 100 mg. of sodium carbonate, with 2 g. of moist fibrin added to each flask, after bringing the temperature in each case up to 40°. Incubation was continued until practically all the fibrin had been digested, which required the following times, in minutes, in different experiments:

A 8 to 15 minutes, B 13 to 25, C 50 to 70, D 75 to 100, E 160 to 180, F 140 to 160.

There is, therefore, a very great difference between the different products when measured in this way, and the findings vary with the degree of disintegration of the fibrin and the frequency with which the flasks are shaken during the digestion. Our fibrin was ground very fine in a meat chopper. With large flakes the digestion is much slower.

The same ferments were mixed in amounts of 100 mg. with 5 g. of a different fibrin in 50 cc. of water, plus 100 mg. of sodium carbonate. The digestions were continued through 3.5 hrs. at 40°. At the end of the time the contents of each flask was slightly acidified with acetic acid and boiled, then filtered. The soluble nitrogen was found in the filtrates, and was as follows, corrected in each case by the nitrogen found in a blank with dead ferment:

A 196.3,   B 137.5,   C 126.3,   D 119.3,   E 73.1,   and F 119 0 mg.

Kjeldahl determinations on three samples of the fibrin gave the amount of total nitrogen in 5 g. equal to 274.4, 278.6, and 274.4 mg.

The results for fibrin A show that about 72% of the substance had been digested to an advanced stage, as the neutralization precipitate had been filtered out here and in the other cases. But these results are not comparable with those of the other digestion; they are given to show the practical difficulty in making such comparisons with fibrin.

In another set of digestions with 5 g. of a fibrin containing 216 mg. of nitrogen, and the same amounts of ferment as before, we found these weights of soluble nitrogen, not diminished by the neutralization precipitate, but otherwise corrected. The digestions were continued 4 hrs. here:

A 209.5,   B 204.4,   C 173.9,   D 148.4,   E, 100.2, and F 157.1 mg.

It appears that nearly the whole of the fibrin was made soluble by Ferments A and B. Comparing the results with those secured in the short periods with 2 g. of fibrin, it is evident that here the major part of the digestion is completed in a period much below 3 or 4 hrs. The effect of the long digestion is to make the weaker products appear *relatively* stronger and nearly as good as the others.

To compare these digestion results on fibrin with the milk and casein tests we shall take the first series and reduce the results to the basis of milligrams of fibrin, with about 25% of dry protein, made soluble in 10 minutes by 1 mg. of ferment. We use the last figures in each case, that is, those representing the longest digestion times:

A gave 53.2, B 32.0, C 11.4, D 8.0, E 4.4, and F 5.0 mg. of fibrin for 1 mg. of ferment.

The same general order appears here as in the other methods of valuation, but the steps are not separated by the same distances.

The general relations for all the methods are shown in Table V, as follows, in which the units of comparison are:

(1) For the metacasein reaction: parts of milk brought to the onset stage by 1 part of ferment in 5 minutes;

(2) Sodium caseinate digestion, Fuld-Gross method: milligrams of casein digested in 1 hr. by 1 mg. of ferment to the point where no precipitate is given by the acetic acid reagent;

(3) The formaldehyde titration. the relative amounts of alkali required to neutralize the amino acids from 1 g. of casein in 2 hrs. digestion,

(4) The fibrin digestion: milligrams of fibrin digested to the soluble stage by 1 mg. of ferment in 10 minutes.

TABLE V

Ferment	Metacasein reaction	Fuld-Gross test	Formaldehyde titration	Fibrin digestion
A	12500	120	100	53 2
B	3400	90	38	32 0
C .	2050	75	38	11 4
D	1520	60	38	8 0
E	1480	40	36	4 4
F	1060	55	33	5 0

This tabulation brings out clearly the lack of uniformity in the behavior of the six ferments in the four reactions   While the tests agree in showing approximately the position which each ferment holds in the series they do not agree as to relative quantitative value   For example, Ferments A and B are far apart in the first test but not so far in the last, and Ferment F actually appears stronger than E by two of the tests, while by the others it is weaker.

What is the explanation of this? We believe this must be sought in two directions. These pancreas preparations are mixtures of several ferments and among them there are probably at least two which have proteolytic properties. It is the common experience of manufacturers of ferments that the pancreases themselves present very different degrees of activity, and investigators have noted the same fact.[1] Further differences are developed by methods of extraction and activation employed. Some manufacturers hold that activation by the addition of parts of the intestine is necessary while others do not make this addition at all. The proferments become activated in very different degrees in this manner and possibly some do not become activated at all. It is plain that variations creep in from the very beginning of the manufacturing treatment, and it is inevitable that the finished products should differ, not only quantitatively, but also qualitatively. We have no definite scientific definition of what trypsin really is, and we do not usually take into account that apparently fundamental differences in behavior sometimes result from the presence of quantities of inorganic salts in the finished products of the market. The process followed by each manufacturer is a secret carefully

[1] Gulewitsch, Z physiol Chem, 27, 540 (1899)

guarded, which provides a situation that obliges the investigator of such products to work in the dark.

The differences in behavior toward acids and toward temperature elevation which have been noted by different workers[1] may probably be traced to the salt content of the different preparations and especially to the relations between the phosphates present. We find that in heating these trypsins their behavior changes in marked manner. In aqueous solution they were all very sensitive to heat and an elevation of temperature to 60° for even 5 minutes brought about great alterations in some respects. For the metacasein reaction 55° is an excessive temperature, as illustrated by the following results where the weights of ferments required to bring about the onset are given·

<div align="center">A 180,   B 80,   C 120,   D 80,   E 160   and F 160 mg.</div>

While the ferments are all enormously weakened the interesting fact is shown that they do not suffer at all in the same manner. Some are much more thermostable than others.

In the Fuld-Gross reaction, using all quantities as employed in the regular test, we find these digestive values for 1 hr. incubation, the ferments having been heated previously to 55°:

<div align="center">A 1 to 33,   B 1 to 24,   C 1 to 22,   D 1 to 23,   E 1 to 11   and F 1 to 15</div>

Here, also, there is exhibited a weakening effect, but in far less marked degree than before. While for A the value in the Fuld-Gross reaction is reduced fourfold, in the metacasein reaction it is reduced forty-fivefold. For the other ferment the changes are in very different degrees. This peculiar behavior suggests that different ferments are concerned in the two reactions, the one which is active in digesting the casein being relatively thermostable. There are other observations which suggest the presence of a mixture of ferments in the pancreas preparations and in earlier work we have noticed this with reference to the behavior toward acids. That a mixture of ferments must be concerned in some of the phenomena observed has been suggested by Sörensen[2] and Edie.[3]

It was hoped at the outset of these investigations that it might be found possible to translate tryptic activity as expressed in terms of one standard into terms of another but this does not appear likely, with our present knowledge, because of the presence of mixtures of bodies with unknown properties in the various preparations as practically dealt with. The translation of standards is possible in a general way only, and the tables above gave some idea of the extent to which this is possible. But, while this hope of finding uniform relations can not be realized at present, the studies permit us to make some positive suggestions as to the necessity

[1] Long and Johnson, THIS JOURNAL, **35**, 1188 (1913); Edie, *Biochem. J*, 8, 84 (1914).

[2] *Biochem Z*, **21**, 300 (1909)

[3] *Loc cit*

of having a better understanding as to the nature of the processes employed in making our commercial preparations. Trypsin must ultimately be defined as a product made in some definite manner and as containing enzymes having definite effects. The trypsin of the physiologist is not much more clearly defined than is the product of the manufacturer. In the statement of properties and behavior put out by the latter there must be some information concerning the content of inorganic substances present, which are doubtless essential factors from certain points of view A statement of the [H] (or [OH]) concentration in aqueous solution with a certain percentage strength would be of value here and would assist greatly in understanding the reactions referred to by different authors. An illustration of this is found in the interesting experiments of Edie, referred to above, where the substratum was a liquid in some of the cases of ferments described. The ferments themselves made up but a small portion of the liquids used, but there is no information as to the rest of the substance present. Without such information regarding reaction or salts present it is not possible to account for some of the singular results obtained with reference to the behavior toward heat or acids. In our work we have avoided some of this uncertainty by employing relatively strong solid products, where quantities of milligrams only came into play, but we have recognized the need of more information even here. Below, a suggestion will be made as to how this more definite information may be secured.

Resume.

(1) In this paper a comparison of the proteolytic value of six pancreas preparations has been made by four distinct methods, the metacasein reaction, a modification of the Fuld-Gross reaction, the formaldehyde titration of amino acids liberated in digestion, and the fibrin digestion. It was hoped to find such relations as would permit the translation of activity as expressed on a given standard in terms of another.

(2) By the four methods the activities of the six preparations are arranged in the same general order, that is, the strongest ferment by the first method is found to be the strongest by the others. For the weakest preparations the order is about the same.

(3) But the relative rank quantitatively, of the different ferments is very different as measured by the different methods. While the strongest ferment by the metacasein reaction appears to be about 12 times the strength of the weakest, and about 10 times as strong by the digestion of fibrin, by the other tests the relation is as 2 or 3 to 1. Even greater irregularities appear in comparing some of the other ferments.

(4) It is not possible at the present time to translate the proteolytic value of a tryptic ferment from the terms of one standard to the terms of another, with the products as at present furnished by chemical or phar-

maceutical dealers, because these preparations are made by very different processes of extraction, concentration or activation, which leave, probably, mixtures of ferments in widely different proportions in the finished products, and unknown amounts of inorganic salts.

(5) There is evidence to suggest that the products sold as trypsins or pancreatins contain at least two different enzymes reacting in different ways with proteins. The effects observed in any case are mixed effects depending on the proportions in which the enzymes are present. These enzymes possess different degrees of thermostability.

(6) The desirability of a more rational definition of trypsin is pointed out. The definition should include a statement of the essential points of manufacture and should be authorized by some responsible body such as a pharmacopoeial revision committee. Since what is called trypsin is prepared for the use of medical men, these users are entitled to the fullest knowledge concerning the composition and properties of the product There is no excuse for secrecy here and products should be made to conform to interchangeable standards.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,
CHICAGO ILL

STUDIES ON ENZYME ACTION. XI. SOME EXPERIMENTS WITH CASTOR BEAN UREASE.

BY K GEORGE FALK AND K. SUGIURA.
Received August 5, 1914.

Takeuchi,[1] in 1909, found in soy beans an enzyme, urease, capable of hydrolyzing urea into ammonia and carbon dioxide. Keisel[2] and Zemplen[3] then showed that ureases are present in a number of plants. The action of the soy bean urease under various conditions was studied by Takeuchi, Armstrong and Horton,[4] Armstrong, Benjamin and Horton,[5] and more recently by Van Slyke, Zacharias, and Cullen.[6] The application of the soy bean urease to the quantitative determination of urea was first proposed by E. K. Marshall, Jr.[7]

In view of the interest which has been developed in connection with the soy bean urease and its application to analytical work, some experiments

[1] *J. Coll Agric , Tokyo*, 1, 1 (1909)

[2] *Z. physiol Chem* , 75, 169 (1911).

[3] *Ibid* , 79, 229 (1912).

[4] *Proc Roy Soc Lond.*, (*B*) 85, 109 (1912)

[5] *Ibid* , 86, 328 (1913)

[6] *Proc Soc Exp Biol Med* , 11, 155 (1914)

[7] *J. Biol. Chem* , 14, 283 (1913); 15, 487, 495 (1913), 17, 351 (1914), 18, 53 (1914) (with D. M Davis) For the quantitative estimation of urea by urease, cf. also Plimmer and Skelton, *Biochem J.*, 8, 70 (1914)

with the urease which was shown to exist in castor beans[1] were carried out and will be described in this paper

Two castor bean preparations were used   Preparation A, consisting of ground, cold pressed, castor beans[2] containing probably about 5% of oil and Preparation B, consisting of husk- and oil free castor beans, ground to pass through a 40 mesh sifter   In the experiments, the castor bean preparation was mixed with the urea solution and water or salt solution and after about 1 cc toluene had been added, allowed to remain in the incubator at 38–40° for the length of time indicated   The ammonia formed was removed by aeration[3] for two or three hours after enough 2 N NaOH solution had been added to make the mixture about 1 N (with respect to the NaOH)   The ammonia was absorbed in the usual way in a definite volume of standard sulfuric acid which was afterwards titrated with standard NaOH solution, with alizarin sulfonic acid as indicator   Preliminary experiments showed that neither the urease preparations nor the urea solutions evolved ammonia in the aeration with normal NaOH solution as described   The urea used contained nitrogen (Kjeldahl determinations) corresponding to 93 8% pure urea, which was therefore used as the basis for calculating the contents of the solutions   The detailed results of the experiments will not be given here but only the percentage amounts of urea hydrolyzed under the conditions of the experiments   The castor bean preparations show very much less activity than do soy bean preparations, so that the reactions were allowed to run considerably longer times than is customary with the latter   For instance, 2 cc of a soy bean extract prepared according to Marshall's method, 100 cc water, 28 1 mg urea, after 4 hours gave 13% hydrolysis, while 10 cc of the filtrate from 10 g of Preparation A and 100 cc water, with 28 1 mg urea and 5 cc water after 18 hours showed 10% hydrolysis   Also, 0 1 g husk- and oil-free, ground, soy beans hydrolyzed 47 mg urea in 50 cc of water completely in 4 5 hours, while 0 2 g Preparation B hydrolyzed only 3 4% of the urea under similar conditions in 25 hours

In the results which follow, the description of the experiments will be given and then the percentage hydrolyses of the urea

Preparation A, 0 5 g , 25 cc solution, 28 1 mg urea, 22 hours

Water, 4 5%, 0 002 N NaOH solution 3 5% 0 002 N HCl solution 1 3%, 0 004 N solution 2 5% 0 004 N HCl solution 1 0%

Dilute HCl and NaOH solutions retard the action, the former to a greater extent than the latter   The retarding actions of strong acids and alkalies, in more than very small quantities, on the action of the soy bean urease, were studied by Takeuchi, Armstrong, Marshall, and Van Slyke

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[1] IV paper of this series, THIS JOURNAL, **35**, 292 (1913)

[2] Supplied by the Baker Castor Oil Company, New York

[3] Köber, THIS JOURNAL, **30**, 1131 (1908), **32**, 689 (1910), Folin and Farmer, *J Biol Chem*, **12**, 499 (1912)

Preparation A, 1 g.; 20 cc. solution; 28.1 mg. urea; 22 hours.

Water, 12%; 0.004 M MnSO$_4$ solution, 10%; 0 075 M Na$_2$HPO$_4$ solution, 14%; 0 04 M MgSO$_4$ solution, 12%; 0 075 M KH$_2$PO$_4$ solution, 3%; 0 075 M NaF solution, 2%.

The disodium phosphate exerted a small accelerating action, while the magnesium and manganous sulfates caused very little change. This latter is of interest in showing that the hydrolytic action of the urease of castor beans is different from the hydrolytic actions of the lipases of castor beans, which are very much accelerated by manganous and magnesium sulfates [1] On the other hand, the retarding influence of sodium fluoride is shown both with the urease and the lipase.[1] Takeuchi found a similar action with the soy bean urease.

Preparation B, 0 5 g , 15 cc. solution; 28 1 mg. urea, 19 hours.

Water..	21%	0.0007 N NaOH sol	16%	0 007 N Na$_2$CO$_3$ sol	21%
0 0007 N HCl sol	19%	0 007 N NaOH sol	15%	0 07 N Na$_2$CO$_3$ sol	20%
0 007 N HCl sol	10%	0 07 N NaOH sol	9%	Water + 1 g CuSO$_4$ -	
0 07 N HCl sol	6%	0 0007 N Na$_2$CO$_3$ sol	18%	5H$_2$O	1%
				Water + 1 g Pb(NO$_3$)$_2$	3%

In the most dilute (0.0007 N) solutions, the HCl exerted a smaller retarding effect than the NaOH, in the more concentrated, the reverse was the case, the actions then being similar to those observed with Preparation A. Sodium carbonate appeared to exert very little influence on the reaction, due, perhaps, to compensating actions in which accelerating effects of carbon dioxide, similar to those observed by Armstrong with the soy bean urease, may play a part The inhibiting actions of copper sulfate and lead nitrate are very marked and similar to the results obtained by Takeuchi with copper sulfate and soy bean urease.

Preparation B, 0 5 g ; 25 cc. solution, 28 1 mg urea, 18 hours

0 1 M Na$_2$HPO$_4$ solution. . . .	23%	0 002 M MnSO$_4$ solution	15%
0 1 M KH$_2$PO$_4$ solution .	6	0 05 M MgSO$_4$ solution	18
0 1 M NaF solution	5		

The results are similar to those obtained with Preparation A. No experiments with water alone were carried out with this series, but to judge from a number of other experiments, 20% of the urea would have been decomposed with no salt present. The slightly alkaline disodium phosphate accelerated the reaction, the acid monopotassium phosphate retarded it almost as much as did the sodium fluoride, while the manganous and magnesium sulfates showed small retarding actions. That manganous sulfate in more concentrated solution exerted considerable retardation is shown by the following results·

Preparation B, 0 5 g , 20 cc water (with added salt), 28 1 mg urea, 23 hours

| No MnSO$_4$ 4H$_2$O added | 19% | 0 05 g MnSO$_4$ 4H$_2$O added | 10% |
| 0 005 g MnSO$_4$ 4H$_2$O added | 15 | 0 04 g MnSO$_4$ 4H$_2$O added . | 6 |

[1] Cf. V paper of this series, THIS JOURNAL, 35, 601 (1913) and the references given there.

The following tables show the results obtained when the quantity of urea, of water, and of the duration of the reaction were varied.

Preparation B, 0 5 mg.; 100 cc. water; duration of reaction, 24 and 48 hours; amounts of urea, as stated

	470	375	282	188	94	47	mg urea
24 hours	0 8	1 2	1 6	2 5	5 2	11 2%	urea hydrolyzed
48 hours	1 3	1 9	2 6	4 3	8 2	14 8%	urea hydrolyzed

For the 24 hours reactions, the absolute quantities of urea decomposed increased with increasing dilution of the solution or decreasing amounts of urea present. For the 48 hours actions, the absolute quantities of urea which were decomposed increased as the dilution increased, down to the concentration of 188 mg., and then decreased on further dilution. The percentage decomposed, however, increased throughout with decreasing concentration. With the soy bean urease, Armstrong and Horton found that increasing the concentration of the urea retarded the reaction, and Marshall, that the velocity of hydrolysis increased with dilution to a maximum and, on further dilution, decreased.

Preparation B, 0 5 g ; 56 3 mg urea; duration of reaction and amount of water, as stated

	100 cc.	80 cc.	60 cc.	40 cc.	20 cc.	10 cc. water
21 hours	4	6	6	7	9	9% urea hydrolyzed
45 hours	8	11	12	14	14	15% urea hydrolyzed
69 hours	13	17	23	25	26	27% urea hydrolyzed

The amount of urea hydrolyzed is very nearly proportional to the time of reaction in most of these experiments. Practically no difference is observable between the results for the most concentrated solutions. The experimental error is comparatively large here, so that the calculation of reaction velocity constants would furnish conclusions of questionable value The relation between any two of these results does not come out clearly, but the trend of the changes when all of the experiments are considered is quite clear.

Preparation B, 0 5 g , 15 cc water, duration of reaction and amount of urea, as stated

	20	43	68	91	115	139	163	187 hours	
14 1 mg urea	30	70	88	95	95	89	.	,	% urea hydrolyzed
28 1 mg urea	16	39		54	62	65	74		% urea hydrolyzed
56 3 mg urea.	10	22	29	34	37	43	40	44%	urea hydrolyzed

With the smallest quantity of urea, the reaction proceeded so far that in most of these results comparison with the rest is not feasible. The products of the reaction, as well as the deterioration of the enzyme due to long contact with water, probably affect these results. These secondary influences show themselves in the third series, where the reaction apparently comes to a stop. All that can be said with regard to these results is that for the first two time periods, the amounts of urea decomposed are nearly proportional to the durations of action, but that variations

occur for greater durations, due to complicating or secondary reactions.

A series of experiments was carried out in which 10 g. of Preparation A were extracted with 100 cc. of solution, filtered through paper, and 10 cc. of the filtrates tested, each with 28.1 mg. urea, 5 cc. of added water, for 18 hours.

Extracting sol.. Water, 1 M NaCl, 0.05 M MgSO$_4$, 0.1 M Na$_2$HPO$_4$, 0.1 M KH$_2$PO$_4$.
% Urea
hydrolyzed: 10   6   8   7   1

Water extracted more urease apparently than the disodium hydrogen phosphate solution, although the solid preparation tested directly with the solutions showed greater activity with the latter than with the former. From the previous results it was to be expected that the monopotassium phosphate extract would show little activity, and that the other salt extracts less activity than the aqueous extract.

Conclusions.

Castor bean preparations hydrolyzed much less urea under comparable conditions than did similar soy bean preparations. This indicates that the urease of castor beans is less active than that of soy beans, or that less urease is present in castor beans than in soy beans.

The action of acids, bases, and salts on the hydrolysis of urea by castor bean urease was studied. Relations, similar to those observed by others with soy bean urease, were found.

ENZYMES PRESENT IN ALFALFA. ALFALFA INVESTIGATION, V.

BY C A. JACOBSON AND AUGUST HOLMES
Received August 14, 1914.

The present work is a continuation of that begun by one of us in Prof. Hedin's laboratory in Uppsala, on the enzymes present in alfalfa seeds.[1]

The same general methods of work there used have been followed in the present investigation, which embraces the enzymes of the green as well as of the dried stems and leaves and of the fresh roots. In addition to the enzymes tested for and determined in the seeds, we have included three carbohydrases not infrequently encountered in juices and extracts of plants, namely, maltase, lactase, and pectinase. All standard solutions employed in the investigation were derived titrimetrically from normal hydrochloric acid, which had been standardized, gravimetrically, against silver.

All experiments were run in duplicate, of which only the mean will be recorded.

[1] THIS JOURNAL, 34, 1730 (1912).

Enzymes in the Dried Stems and Leaves.

A water extract of air dried and finely ground alfalfa hay of the same quality as that used in Alfalfa Investigation I[1] and II[2] was prepared by adding 400 g. water to 100 g. of the ground alfalfa, and then heating the well stirred mixture for two hours at 37°, pressing out the extract in a small hand press and filtering through a soft filter paper. The reddish brown filtrate was clear and remained so for several hours, but if allowed to stand over night it became cloudy and a light precipitation was found at the bottom of the containing vessel. In every experiment the clear fresh extract was used.

Lipase —No positive evidence of the existence of a lipase was found in alfalfa seeds and it was hardly to be expected that this enzyme should exist in the other parts of the plant, in measurable quantity. This supposition was also sustained by the following experiments

Experiment 1 —(a) 5 cc ethyl benzoate + 25 cc extract + 50 cc water + a few drops toluene, the mixture heated at 37°, after which 25 cc of the liquid were withdrawn and titrated with 0 5 *N* NaOH, giving 3 04 cc for neutralization

(b) 5 cc ethyl benzoate + 75 cc water, treated the same as in (a) 25 cc of this mixture were then withdrawn and titrated with 0 5 *N* NaOH giving 0 10 cc for neutralization

(c) 25 cc extract + 55 cc H₂O digested and titrated like (b), gave 2 38 cc 0 5 *N* NaOH

The sum of the titration values of (b) and (c) is a little less than (a), therefore a slight saponification of the ester had taken place

Experiment 2 —(a) 5 cc olive oil + 25 cc extract + 50 cc water were heated together as in Expt 1 (a) 25 cc of the resulting liquid were withdrawn and titrated with 0 5 *N* NaOH, giving 3 86 cc for neutralization

(b) 5 cc olive oil + 75 cc H₂O, digested and titrated as in (a), giving 0 12 cc for neutralization

(b) + (c) of Expt. 1 gave a lower value than (a), therefore, a slight saponification of olive oil. From these results we conclude that there is a suggestion of a lipase present in the alfalfa extract to about the same extent as was found in the seeds.

Amylase.—It was found that the alfalfa extract itself reduced an alkaline copper solution, so that this enzyme could only be determined by obtaining the difference of the reducing power with and without starch. No attempt was made to extract and isolate the ferment.

To determine whether or not amylase was present in the extract the following experiment was carried out.

Experiment 1 —(a) 5 cc extract + 50 cc H₂O + 10 cc of a 1% starch solution, and the mixture heated at 60° for one hour, after which it was heated to boiling and filtered

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[1] THIS JOURNAL, **33,** 2048 (1911)

[2] *Ibid* , **34,** 300 (1912)

(b) 5 cc. extract + 65 cc. H₂O, heated as in (a).

(c) 10 cc. starch solution + 55 cc. H₂O, also heated as in (a).

The reducing sugar in the filtrate was determined according to the method of Kendall,[1] the copper being titrated with 0.1 N sodium thiosulfate, which resulted as follows: (a) 26.27 cc.; (b) 23.86 cc.; and (c) none, showing that amylase is present in small amount.

The following experiment was carried out to determine the diastatic power[2] of the extract:

.   *Experiment 2.*—(a) 100 cc. of a 1% starch solution + 1 cc. extract.

(b) 100 cc. of a 1% starch solution + 2 cc. extract.

(c) 100 cc. of a 1% starch solution + 3 cc extract.

(d) 100 cc. of a 1% starch solution + 5 cc extract

The above solutions were heated simultaneously, one hour at 61° and then the reducing sugar determined as above, giving for (a), 20.84 cc sodium thiosulfate solution of such a strength that 1 cc. is equivalent to 8.13 milligrams of copper; (b), 48.54 cc.; (c), complete reduction; and (d), 19.43 cc.

Having obtained the value of the reduction by the pure extract in (d), we are able to find by difference the reduction due to the amylase. This gives (a) 16.95 cc., and (b) 40.76 cc. of thiosulfate solution, or 137.8 mg. of copper in (a) and 331.4 mg. copper in (b). These values of copper are equivalent to 120.4 mg. and 292.3 mg. of maltose, respectively, making the diastatic power 24 and 33 in the two cases, or a mean diastatic power of 28.5.

Coagulase.—Having found this enzyme in the alfalfa seed extract, it was of interest to learn if it also occurred in the stem and leaves of the dried plant.   Fresh milk was taken and treated with one-tenth its volume of a 20% solution of calcium chloride and then treated with the extract as given in the following experiment:

Experiment 1.—(a) 10 cc prepared milk + 1 cc extract

(b) 10 cc. prepared milk + 1 cc. water.

(c) 10 cc. prepared milk + 0 5 cc 0 1 N acetic acid

(d) 10 cc prepared milk + 0.5 cc 0 1 N n-butyric acid.

The two latter representing an excess of the amount of acidity developed in 1 cc. of extract during 24 hours' digestion.   The above mixtures were then heated in the incubator at 37° for 24 hours and the process of change watched from time to time during that period.   No marked change took place and at the end of 24 hours the milk could quite easily be poured, showing that there is no coagulase, on the order of rennin, in the alfalfa extract.

Emulsin.—This enzyme is determined by its power of splitting up the glucoside amygdaline into glucose, benzaldehyde and hydrocyanic acid

[1] THIS JOURNAL, **24**, 317 (1904)

[2] If 1 cc. of amylase solution develops maltose equivalent to 500 mg. of copper when digested with 100 cc of a 1% starch solution it is said to have a diastatic power of 100.

and the estimation of any one of the decomposition products. Whether or not the enzyme is a typical amygdalase containing hydroxynitrilase and yielding mandelonitrile glucoside as an intermediate product we did not consider of sufficient importance for the present investigation. We at first attempted to determine the emulsin by titrating with iodine, the hydrocyanic acid generated, but were obliged to abandon this procedure for the reason that the extract itself absorbs considerable quantities of iodine. The determination of the glucose was therefore resorted to, and the results given in the following experiments:

Experiment 1 —(*a*) 25 cc extract + 0 25 g amygdaline + 25 cc H₂O

(*b*) 25 cc extract + 25 cc H₂O

(*c*) 0 25 g amygdaline + 25 cc H₂O

(*d*) 0 05 g. Merck's emulsin + 0 25 g amygdaline + 25 cc. H₂O

All four portions digested for 24 hours at 37° and the reducing power of 5 cc of the supernatant liquid used for the determinations, which resulted as follows

(*a*) 16 20 cc sodium thiosulfate solution were required to titrate the reduced copper (*b*), 10 60 cc , and (*d*), 3 22 cc   In (*c*) there was no reduction

These results are not quantitative in character, but suffice it to say, that emulsin is present in considerable quantity in the dried leaves and stems of alfalfa.

Invertase.—To determine the presence of invertase the following experiments were carried out:

Experiment 1 —(*a*) 2 cc of 10% cane sugar solution + 5 cc extract + 50 cc H₂O.

(*b*) 5 cc extract + 52 cc H₂O

(*c*) 2 cc —10% cane sugar solution + 5 cc 0 2 *N* HCl + 50 cc H₂O

(*d*) 2 cc 10% cane sugar solution + 0 83 cc 0 2 *N* HCl + 50 cc H₂O

(*e*) 5 cc extract + 5 cc 0 2 *N* HCl + 50 cc H₂O

The above solutions were heated for 24 hours in the thermostat at 37° and then brought to boiling and filtered. The reducing sugar in the filtrate was determined by Kendall's method. By a previous experiment it was found that 5 cc. of the extract heated under the same conditions developed an acidity equivalent to 0.83 cc. 0.2 *N* HCl and hence the reason for the (*d*) part of the experiment. In terms of cubic centimeters of standard thiosulfate solution, the reducing sugar obtained from the above solutions was found to be

(*a*)—57 51 cc , (*b*)—25 14 cc , (*c*)—35 21 cc., (*d*)—23 00 cc ; (*e*)—24.18 cc

It is seen that the value of (*a*) is larger than the sum of (*b*) and (*d*) which indicates the presence of invertase. From part (*c*) we see that even 5 cc. 0.2 *N* HCl does not produce as large an inversion of cane sugar as the same volume of alfalfa extract.

It was then decided to try the action of the enzyme in neutral solution and the following experiment carried out:

Experiment 2 —(*a*) 2 cc 10% cane sugar solution + 5 cc extract + 50 cc H₂O + excess of powdered CaCO₃

(*b*) 5 cc extract + 52 cc. H₂O + excess of powdered CaCO

The titration of the reduced copper in presence of an excess of potassium iodide resulted as follows: (*a*) 42.50 cc., and (*b*) 22.30 cc. sodium thio-sulfate solution, showing that an active invertase is present in neutral solution of the alfalfa extract.

Peroxidase.—The tests for oxidases and peroxidases were carried out as follows:

Experiment 1 —(*a*) 1 g pyrogallol + 1 cc extract + 10 cc of a 1% H_2O_2 solution diluted to 50 cc with water

(*b*) Same as (*a*), except no H_2O_2, also diluted to 50 cc There was no change in (*a*) or (*b*) even after standing over night

Experiment 2 —(*a*) A guaiacum emulsion, obtained by dissolving a small amount of gum guaiacum in alcohol and adding water until a cloudiness appeared, + 1 cc extract + 3 cc of a 3% solution of H_2O_2 and the mixture diluted to 10 cc with water

(*b*) Same as (*a*), without the H_2O_2, also diluted to 10 cc A bluish precipitate developed in (*a*) after standing for a few minutes, which became heavier upon longer standing There was no change in (*b*) until next morning when a very light, bluish precipitate had settled out

These experiments go to show that no oxidase, but an extremely small amount of a peroxidase is present in the alfalfa extract. No test could be made with cresol for lack of this reagent.

Maltase.—To investigate whether maltase was present or not the following method was employed: The optical activity of a maltose solution was observed before and after digesting with a portion of the extract.

Experiment 1 —(*a*) Rotation of a 2% maltose solution, + 2 54°

(*b*) Rotation of a mixture of 50 cc of 2% maltose solution + 10 cc extract before digestion, + 2 05°

(*c*) Rotation of same mixture as (*b*), which had been digested 24 hours at 37°, + 1 84°

The change in rotation is so slight that we would scarcely be justified in saying that maltase is present in the extract.

Lactase —*Experiment 1* —(*a*) The rotation of a 2% lactose solution was found to be + 1 03°

(*b*) Rotation of a mixture of 50 cc 2% lactose solution + 10 cc. extract before digestion, + 1 01°

(*c*) Rotation of the same mixture as (*b*) after digesting for 24 hours at 37°, +0 89°.

The small change in rotation would scarcely warrant the statement that a lactase is present

Pectinase.—A good grade of pectin was prepared from dried pears by the following method: About 4 pounds of dried pears were passed through a meat chopper and soaked in enough water to cover the same, for about 14 hours at room temperature, and the resulting infusion separated by decantation and pressing and finally filtration. The clear amber colored filtrate was freed from calcium and albuminates by precipitating with oxalic acid and tannin and the solution again filtered. It was then concentrated on the water bath to about one-third of its original volume

and after cooling to the room temperature the pectin was precipitated by adding gradually, with constant stirring, three to four volumes of 95% alcohol. The thick, gelatinous precipitate was separated by filtering through an ordinary filter paper. As this was a very slow process, the filtration was arranged to proceed over night and the following day. The small, brown and horny looking material left in the filter papers, was then dissolved in a small quantity of water and the precipitation with 95% alcohol repeated. The process was repeated four times after which the gelatinous precipitate resulting was almost a pure white, but when dry it was dark, and its properties suggested dried glue, although the pectin was not quite so elastic.

An equal volume of extract was added to a 2% solution of this pear pectin. The mixture gelatinized almost instantaneously, showing the presence of a pectinase in considerable quantity in the water extract of dry alfalfa hay.

Protease.—In the paper[1] already referred to, the discovery of a pepto-lytic enzyme, on the order of vegetable erepsin, in alfalfa seed, is recorded; but this protease is not a peptonizing one like pepsin. It was, therefore, of considerable interest whether or not the presence of a similar enzyme could be confirmed in the extract of the dried plant.

Digestion experiments were set up with extracts on egg albumin, serum albumin, and fibrin, similar to those carried out on the seeds, the results in every case turning out negative.

The following experiments were then arranged to see if casein and Witte peptone could be digested with the extract. Solutions of these modified proteins were prepared exactly as specified in the paper just mentioned, with the exception that the casein solution required only 9.5 cc. N NaOH for neutrality to litmus instead of 10 cc.

Experiment 1 —(a) 25 cc extract + 50 cc casein solution + 1 cc toluene.
(b) 25 cc. extract + 50 cc water + 1 cc toluene
(c) 50 cc casein solution + 2ᵣ cc water + 1 cc toluene
(d) 25 cc (boiled) extract + 50 cc casein solution + 1 cc toluene
(e) 25 cc. (boiled) extract + 50 water + 1 cc toluene

The above mixtures were digested 24 hours at 37°, after which 25 cc. of the supernatant liquid of each were withdrawn, 50 cc. water and 10 cc. neutral formol phenolphtnalein solution[2] added to each and the mixtures titrated with 0.2 N NaOH solution, resulting as follows: (a) 6.47 cc., (b) 2.72 cc., (c) 1.22 cc., (d) 3.30 cc., and (e) 2.35 cc.

Experiment 2.—(a) 25 cc. extract + 50 cc. 2% peptone solution + 1 cc toluene.
(b) 25 cc. extract + 50 cc. water + 1 cc. toluene
(c) 25 cc. water + 50 cc. peptone solution + 1 cc. toluene

[1] THIS JOURNAL, 34, 1734 (1912).
[2] Made by adding 1 cc. of a 1% alcoholic phenolphthalein solution to 50 cc. of a 40% formaldehyde solution and titrated to a faint pink with 0 5 N NaOH

(*d*) 25 cc. (boiled) extract + 50 cc. peptone solution + 1 cc. toluene.

(*e*) 25 cc. (boiled) extract + 50 cc. water + 1 cc. toluene.

The mixtures digested and titrated as in Expt. 1, with the following results: (*a*) 5.82 cc., (*b*) 2.70 cc., (*c*) 1.80 cc., (*d*) 4.31 cc., and (*e*) 2.33 cc. These two experiments go to show that the extract of the dried alfalfa as well as that of the seeds, contains a protease capable of splitting up both casein and peptone.

Reaction Influence.—Experiments were arranged to determine whether or not the action of the protease would be influenced by an acid or alkaline solution, which was found to be the case with the seed protease.

Experiment 1.—(*a*) 25 cc extract + 50 cc H_2O + (toluene)

(*b*) 25 cc extract + 50 cc casein solution + (toluene)

(*c*) 25 cc extract + 50 cc casein solution + 0 5 g sodium carbonate.

(*d*) 25 cc extract + 50 cc. casein solution + Na_2CO_3 to make a 0 5% solution.

(*e*) 25 cc extract + 50 cc casein solution + Na_2CO_3 to make a 1 0% solution

(*f*) 25 cc extract + 50 cc casein solution + Na_2CO_3 to make a 2% solution

(*g*) 25 cc water + 50 cc extract

The mixtures were digested for 24 hours at 37°, after which the calculated amount of N HCl was added to neutralize the Na_2CO_3 in each portion, and the liquids titrated as before, making due allowance for the volume change upon neutralization of the carbonate. (*a*) gave 1.56 cc. of 0.2 N NaOH, (*b*) 3.42 cc., (*c*) 4.97 cc., (*d*) 4.82 cc., (*e*) 5.29 cc., (*f*) 7.51 cc., and (*g*) 1.39 cc., showing that an alkaline medium favors the digestion of casein.

Experiment 2 —(*a*) 25 cc extract + 50 cc casein solution + HCl to 0.05% solution

(*b*) 25 cc extract + 50 cc casein solution + HCl to make a 0 1% solution

(*c*) 25 cc extract + 50 cc casein solution + HCl to make a 0 2% solution

(*d*) 25 cc extract + 50 cc casein solution + HCl to make a 0 3% solution

(*e*) 25 cc extract + 50 cc. casein solution + HCl to make a 0 4% solution

The digestions were carried out under the same conditions as those above and then the added HCl exactly neutralized with N NaOH and the formol titration carried out in the usual manner, giving for (*a*) 2.36 cc. 0.2 N NaOH, (*b*) 2.16 cc., (*c*) 2.11 cc., (*d*) 1.84 cc., and (*e*) 1.67 cc., showing that an acid solution acts unfavorably upon the digestion of casein, which was likewise the case with the seed protease.

Influence of Albumin in the Digestion of Casein and Peptone.

It was found that the presence of small amounts of egg albumin or serum in the digestion liquid of seed protease inhibited the action of the enzyme upon both casein and peptone, and therefore experiments were carried out to learn if the action of the plant protease is similarly inhibited.

Experiment 1.—(*a*) 25 cc extract + 10 cc. H_2O + 50 cc casein solution and the mixture titrated at once

(*b*) 25 cc extract + 10 cc. H_2O + 50 cc. casein solution digested at 37° for 24 hours

(c) 25 cc. extract + 50 cc casein solution + 10 cc albumin solution (made by dissolving the white of one hen's egg in 1 liter of water) and the mixture titrated at once

(d) 25 cc. extract + 50 cc casein solution + 10 cc albumin solution digested for 24 hours at 37°

(e) 25 cc. extract + 10 cc albumin solution mixed and left in contact for one-half hour at room temperature, then 50 cc casein sol added, and the mixture titrated at once

(f) Same as (e) except after adding the casein the mixture was digested 24 hours at 37°

(g) 25 cc extract + 10 cc albumin solution allowed to act together for 2 hours at room temperature, then 50 cc casein solution added, and the mixture titrated at once

(h) 25 cc extract + 10 cc albumin solution left 2 hours at room temperature, then 50 cc casein solution added and mixture digested at 37° for 24 hours and titrated

(i) 25 cc extract + 10 cc albumin solution left in contact at room temperature 21 hours, then 50 cc casein solution added and the mixture titrated at once

(j) Same as (i), except after adding casein the mixture was digested for 24 hours at 37° and then titrated

Results of Titrations —(a) 2.93 cc 0 2 N NaOH, (b) 3 36 cc, (c) 2 93 cc, (d) 3 20 cc, (e) 2 94 cc, (f) 3 19 cc, (g) 2 91 cc, (h) 3 14 cc, (i) 2 97 cc (j) 3 05 cc, showing a small but definite inhibitory action of the albumin upon the casein digestion, which is proportional to the time of action

Experiment 2 —(a) 25 cc extract + 10 cc H₂O + 50 cc 2% peptone solution titrated at once

(b) 25 cc extract + 10 cc. H₂O + 50 cc peptone solution heated 24 hours at 37° and then titrated

(c) 25 cc extract + 10 cc albumin solution + 50 cc peptone, titrated it once

(d) 25 cc extract + 10 cc albumin solution + 50 cc peptone, heated 24 hours at 37° and then titrated

(e) 25 cc extract + 10 cc albumin solution left at room temperature for one half hour and then 50 cc peptone added, and the mixture titrated at once

(f) 25 cc extract + 10 cc albumin, left at room temperature for one-half hour, then 50 cc. peptone added, digested at 37° for 24 hours and titrated

(g) Same as (e) except extract and albumin left for 2 hours at room temperature.

(h) Same as (f) except extract and albumin left for 2 hours at room temperature.

(i) Same as (e) except extract and albumin left together for 24 hours at room temperature before adding the peptone

(j) Same as (f) except extract and albumin left together for 24 hours at room temperature

The formal titrations resulted as follows· (a) 3 10 cc 0 2 N NaOH, (b) 4 24 cc, (c) 3 09 cc, (d) 4 22 cc, (e) 3 12 cc, (f) 4 21 cc, (g) 3 05 cc, (h) 4 22 cc., (i) 3 20 cc, (j) 4 24 cc., showing that egg albumin does not perceptibly influence the digestion of peptone by alfalfa protease

A series of experiments were then run to determine whether the time or the temperature plays the greater influence in the inhibition of plant protease on casein by egg albumin, but it would seem unnecessary to reproduce this mass of detail. The results all pointed to the conclusion that it is the time of action and not the temperature that determines the extent of inhibition.

Enzymes in the Fresh Alfalfa Plant (Stem and Leaves).

Young growing plants were collected and ground to a fine pulp in a

meat chopper, and after stirring it up with an equal volume of water, the mixture was allowed to stand for 2 hours at a temperature of 37°, after which the extract was pressed out and filtered. The filtrate was clear and of an amber brown color. Methods identical with the foregoing were employed for the determinations, except in the determination of the reducing sugars, in which cases the cuprous oxide was titrated by means of the ferric sulfate and permanganate method. This method, however, is not to be recommended for such work. The iodometric copper method of Kendall is to be preferred.

Lipase —*Experiment 1* —(*a*) 5 cc ethyl benzoate + 25 cc extract + 50 cc H_2O
(*b*) 25 cc extract + 50 cc H_2O
(*c*) 5 cc ethyl benzoate + 75 cc H_2O
(*d*) 5 cc olive oil + 25 cc extract + 50 cc H_2O
(*e*) 5 cc olive oil + 75 cc H_2O

The titration values are as follows. (*a*) 3.29 cc., (*b*) 2 93 cc., (*c*) 0 11 cc., (*d*) 3.15 cc., (*e*) 0.05 cc., showing that there is a small, but appreciable, amount of lipase present.

Amylase —*Eperiment 1* —(*a*) 5 cc extract + 10 cc starch solution + 50 cc H_2O.
(*b*) 5 cc extract + 60 cc H_2O
(*c*) 10 cc starch solution + 55 cc water

The number of cubic centimeters of permanganate required for the precipitated cuprous oxide were found to be. (*a*) 17.41 cc., (*b*) 15 09 cc., and (*c*) none. Therefore, a small amount of amylase is present.

Coagulase —*Experiment 1* —(*a*) 10 cc prepared milk + 1 cc extract
(*b*) 10 cc milk + 1 cc water
(*c*) 10 cc milk + 0 37 cc 0 1 N acetic acid
(*d*) 10 cc milk + 0 37 cc 0 1 N butyric acid

Results· (*a*), coagulated to a firm mass in seven hours, whereas the others remained practically unchanged, showing that a coagulase on the order of rennin is present.

Emulsin —*Experiment 1* —(*a*) 5 cc extract + 5 cc of a 5% amygdaline solution + 50 cc H_2O
(*b*) 5 cc extract + 55 cc H_2O
(*c*) 5 cc amygdaline solution + 55 cc H_2O
(*d*) 5 cc amygdaline solution + 5 cc of a 0 5% emulsin solution + 50 cc H_2O

The number of cubic centimeters of permanganate required for the cuprous oxide is as follows: (*a*) 28.53 cc., (*b*) 15.30 cc., (*c*) 1.10 cc., and (*d*) 39.34 cc. The results indicate that emulsin is present in the fresh plant to a marked degree.

Invertase.—*Experiment 1* —(*a*) 2 cc 10% cane sugar solution + 5 cc extract + 50 cc H_2O
(*b*) 5 cc extract + 52 cc H_2O
(*c*) 2 cc sugar solution + 55 cc H_2O
(*d*) 2 cc sugar + 2 cc. 0 2 N HCl + 50 cc H_2O.
(*e*) 2 cc sugar + 5 cc extract + 50 cc H_2O + (powdered) $CaCO_3$
(*f*) 5 cc extract + 52 cc H_2O + (powdered) $CaCO_3$

Results: (b), developed an acidity of 1.91 cc. 0.2 N NaOH. The titrations with permanganate were (a) 51.41 cc., (b) 15.10 cc., (c) no reduction, (d) 21.96 cc., (e) 21.45 cc., and (f) 13.18 cc., which indicate the presence of invertase in small amount.

Peroxidase —Experiment 1 —(a) 1 g pyrogallol + 10 cc of a 1'₍ solution of H_2O_2 + 1 cc extract, diluted to 50 cc with water

(b) Same as (a) but without hydrogen peroxide

(c) Guaiacum emulsion + 1 cc extract + 3 cc of a 3'₍ H_2O_2 solution + water to 10 cc

(d) Same as (c), but without the H_2O_2

(e) α-Naphthol + 1 cc extract + 1 cc 3'₍ H_2O_2 + H_2O to 10 cc

(f) Same as (e) but without the H_2O_2

Results: (a), immediately assumed a yellowish brown color, and in a few minutes a heavy brown precipitate appeared. In (b) no change, (c) developed the characteristic bluish precipitate at once, (d) no change for a long time, (e) a violet colored precipitate settled out in a few minutes, (f) remained unchanged. All these facts point to the presence of a peroxidase but not to an oxidase.

Pectinase.—The test for this enzyme with pectin from pears gave a more positive result than with the extract of the dry alfalfa.

Protease (Casein Digestion) – Experiment 1 —(a) 25 cc extract + 50 cc casein solution

(b) 25 cc water + 50 cc casein solution

(c) 25 cc extract + 50 cc water

(d) 25 cc extract (boiled) + 50 cc casein solution

After digestion the formol titration resulted in: (a) 6.80 cc. 0.2 N NaOH, (b) 1.31 cc., (c) 2.95 cc., (d) 4.18 cc., which brings out the fact that a stronger casein digesting ferment is present in the fresh than in the dried plants.

(Peptone Digestion)—Experiment 2 —(a) 25 cc extract + 50 cc peptone solution.

(b) 25 cc extract + 50 cc H_2O

(c) 25 cc. water + 50 cc peptone solution

(d) 25 cc (boiled) extract + 50 cc peptone solution

Titrations were as follows: (a) 7.07 cc. 0.2 N NaOH, (b) 3.29 cc., (c) 1.78 cc., (d) 4.61 cc., showing that peptone is easily digested by the enzyme.

(Egg Albumin Digestion.)—Experiment 3 —(a) 25 cc. extract + 50 cc albumin solution.

(b) 25 cc. extract + 50 cc H_2O

(c) 25 cc. H_2O + 50 cc albumin solution.

The titrations resulted as follows: (a) 3.15 cc., (b) 3.17 cc., (c) 0.12 cc. These results show conclusively that the protease in question is unable to digest albumin, and therefore not a peptonizing enzyme.

Enzymes in the Fresh Alfalfa Root.

Fresh alfalfa roots were dug and ground up in a meat chopper, treated with water, digested for a short time at 37°, and the extract pressed out and filtered. The clear filtrate was used for the following experiments:

Lipase.—*Experiment 1.*—(a) 25 cc. extract + 2 cc. ethyl benzoate + 50 cc. H₂O.

(b) 25 cc. extract + 52 cc. H₂O.

(c) 2 cc. ethyl benzoate + 75 cc. H₂O.

(d) 25 cc. extract + 2 cc. olive oil + 50 cc. H₂O.

(e) 2 cc. olive oil + 75 cc. H₂O.

The titration with 0.2 N NaOH resulted in the following values: (a) 2.48 cc., (b) 2.24 cc., (c) 0.07 cc., (d) 2.26 cc., (e) 0.08 cc., indicating that lipases are absent.

Amylase—*Experiment 1*—(a) 5 cc extract + 10 cc starch solution + 50 cc H₂O.

(b) 5 cc. extract + 60 cc. H₂O.

(c) 10 cc starch + 55 cc H₂O

In these experiments the reduced copper was determined iodometrically and the titrations with sodium thiosulfate resulted as follows: (a) 7.20 cc., (b) 5.85 cc., (c) no reduction, showing that amylase is present although to a less extent than in the stems and leaves.

Coagulase.—Identical experiments with those under coagulase in the foregoing section were set up and after digesting the mixtures for 5 hours at 37°, a thickening of the milk in tube (a) was observed, whereas the milk in the other tubes remained unchanged. This points to the presence of a coagulase in the root extract also.

Emulsin.—Experiments were run on the root extract corresponding to (a), (b) and (c) in the foregoing section, and after heating, the thiosulfate titration resulted as follows: (a) 7.13 cc., (b) 5.80 cc., (c) no reduction. Emulsin is present in very small amount in the roots.

Invertase.—*Experiment 1*—(a) 2 cc. cane sugar solution + 5 cc extract + 50 cc. H₂O

(b) 2 cc. sugar solution + 55 cc H₂O

(c) 2 cc sugar solution + 2 cc 0.2 N HCl + 50 cc. H₂O.

(d) 5 cc extract + 52 cc. H₂O.

(e) 2 cc sugar solution + 1 cc 0.2 N HCl + 50 cc. H₂O.

The thiosulfate titrations resulted as follows: (a) 10.01 cc., (b) no reduction, (c) 22.76 cc., (d) 5.80 cc., (e) 12.40 cc. Invertase is thus present to a limited extent and nearly equivalent to 1 cc. of 0.2 N HCl.

Peroxidase.—The same experiments as (a), (b), (c) and (d), of the foregoing section were carried out using root extract. The results may be given as follows: (a), formed a heavy brown precipitate immediately; (b), remained unchanged; (c), developed a deep blue precipitate immediately; while (d), remained unchanged for several hours. These results indicate that peroxidases are present in the roots to a larger degree than in the stems and leaves, but no oxidases are present.

Pectinase.—The results of the pectinase tests on the root extract resulted positive.

Protease (Casein Digestion).—*Experiment 1.*—(a) 25 cc. extract + 50 cc. casein solution.

(b) 25 cc. H₂O + 50 cc. casein solution.

(c) 25 cc. extract + 50 cc. H_2O
(d) 25 cc. (boiled) extract + 50 cc casein solution.

Formol titrations: (a) 4.52 cc. 0.2 N NaOH, (b) 1.28 cc., (c) 2.23 cc., (d) 4 22 cc. These results indicate that no protease is present in the root extract.

(*Peptone Digestion*)—*Experiment 2* —(a) 25 cc extract + 50 cc peptone solution
(b) 25 cc H_2O + 50 cc peptone solution
(c) 25 cc extract + 50 cc H_2O
(d) 25 cc extract (boiled) + 50 cc peptone solution

The solutions were heated in the usual way and then titrated, giving the following values: (a) 5.33 cc., (b) 2.18 cc., (c) 2.23 cc., (d) 5.36 cc. The values for (a) and (d) are seen to be almost identical in this case also, and therefore no digestion of peptone.

(*Albumin Digestion*)—*Experiment 3* —(a) 25 cc extract + 50 cc albumin solution
(b) 25 cc H_2O + 50 cc albumin solution
(c) 25 cc extract + 50 cc H_2O

After heating, the titrations resulted as follows: (a) 2.38 cc., (b) 0.10 cc., (c) 2.23 cc., showing that no digestion of albumin has taken place.

Conclusion.

The present investigation was designed to cover the more common enzymes encountered in vegetable juices and extracts, but no attempt has been made to isolate the different ones from their media, nor to study them in minute detail. Their presence in the water extracts of the dried and fresh alfalfa stems and leaves, as well as in the alfalfa roots has been determined qualitatively and in some instances with reference to the approximate amount. The following table sets forth the results obtained in the present investigation, together with those obtained on alfalfa seeds:

Enzyme	Dried plants	Fresh plants	Fresh roots	Seeds
Lipase	—	+(s)	—	—
Amylase	+(s)	+(s)	+(s)	+
Coagulase	—	+	+	+
Emulsin	+(l)	+(l)	+(s)	+
Invertase	+	+(s)	+	—
Peroxidase	+(s)	+	+(l)	+
Maltase	—			
Lactase	—			
Pectinase	+(l)	+(l)	+	
Protease (peptonizing)	—	—	—	—
Protease (peptolytic)	+	+	—	+

The presence of the enzyme is denoted by + and the absence by —, the (s) after the sign denotes, in small amount; and the (l) in considerable, or large amount.

The diastatic power of the water extract of the dried plants was determined and found to be approximately 20.

A slight alkalinity favors the action of the protease on casein, whereas

an acid solution above that spontaneously produced in the extract retards or inhibits this action.

No digestion of egg albumin could be detected by the proteases in any part of the plant, but this substance invariably retards the action of the enzyme on casein. It was also found that the inhibiting influence of egg albumin on the casein digestion was proportional to the time of action and not to the temperature.

It is hoped that a more detailed investigation of individual members of the alfalfa enzymes can be undertaken in the near future.

RENO, NEVADA.

THE VOLATILE OIL OF CALYCANTHUS FLORIDUS.

By EMERSON R MILLER, G W TAYLOR AND M H ESKEW

The plant family Calycanthaceae comprises two genera and six or seven species, natives of North America and eastern Asia. The family is represented in the United States by four or five species of the genus *Calycanthus* L. (*Butneria Duhamel*), all but one of which are found in the south eastern states. The remaining one is native to California. All of these are aromatic shrubs from two to ten feet high, growing on hillsides and along streams. The flowers of the eastern species appear early in the spring, are brownish to brownish purple and exhale a delightful fragrance, compared by some to that of strawberry. Owing to their aromatic properties these plants are known commonly as Sweet Scented Shrub, Strawberry Shrub, Carolina Allspice, Florida Allspice, etc. The California species is known also by the names Spice Bush, Spice Wood, Wine Flower, etc. Plants of this latter species are a little larger than the others and have somewhat larger flowers of a livid red color.

Though this genus may not be rightly considered as being of much economic importance, two of its species, namely, *Calycanthus floridus* and *C. fertilis* (*glaucus*) are cultivated as ornamental shrubs both in this country and in Europe. Of further interest may be mentioned its reputed medicinal and poisonous properties. Thus, according to the National Standard Dispensatory, the root, leaves and bark of *C. fertilis* are much used as an antiperiodic. This undoubtedly means as a so-called domestic remedy. Kings' American Dispensatory states that the same species has been suggested as a stimulant, antiperiodic and an aromatic, while the root is said to be emetic. There are also reports of its having been poisonous to cattle. Other writers on medicinal plants include also the *C. floridus*. With the exception of the single phytochemical group of alkaloids practically nothing is known of the chemistry of this genus.

In 1888 the alkaloid calycanthine was discovered in the seeds of *Caly-*

canthus glaucus by R G Eccles[1] and a year later his work was confirmed by H W Wiley[2] who separated also about 47% of a fixed oil   Since then several papers have been published by H M Gordin[3] who has shown that two alkaloids, calycanthine and isocalycanthine occur in the seeds

\ccording to the experiments of A R Cushney[4] on the pharmacological action of calycanthine, its effect on the spinal cord is about the same as that produced by strychnine poisoning, though the spasms are shorter

In mammals, calycanthine seems to act as a stimulant to the spinal cord and as a depressant to the heart   In frogs it has, in addition, a weak, curare like action on the terminations of the motor nerves   The symp toms are so similar to those described in cattle from poisoning from calycanthus that there can be no doubt that the alkaloid is the chief poisonous constituent "

In 1912 Mirande[5] reported finding in 100 parts of fresh leaves of *C alycanthus floridus* 0 004 of HCN, the same amount in 100 parts of the leaves of *C laevigatus*, and 0 016 in 100 parts of leaves of *C occidentalis*

In 1912 H W Brooks[6] examined the roots, leaves and flowers of *C floridus* for alkaloids and obtained results which make the presence of alkaloids very probable, especially in the leaves

Experimental.

The volatile oil used in this investigation was separated by steam distillation from material collected mainly in the vicinity of Auburn, Ala According to the 'Flora of the Metamorphic Region of Alabama ' by F S Earle our material consisted mainly, if not entirely, of *Calycanthus floridus*   Most of the material was collected after the leaves had fallen, but any leaves still remaining were removed   The shrubs were cut off just above the ground, allowed to become air dry, coarsely comminuted and then distilled with steam

Three samples of oil were obtained, one in 1908–09, one in 1909–10 and another in 1911 12   The yield was 0 53%, 0 25% and 0 39%, respectively The smaller, younger plants gave the best yield   This might be expected, since most of the oil is found in the bark, especially in that of younger stems

Physical and Chemical Properties of the Oils —In general appearance these oils were very similar, of a light yellowish color, a warm aromatic taste and a pleasant, refreshing camphoraceous odor suggestive of cineol

Proc Am Pharm Assoc **36**, 84 and 382 (1888)

Am Chem J **11**, 557 (1889)   *Am J Pharm* **62**, 96 (1890)

[3] *Proc Am Pharm Assoc* **52**, 345 (1904) *Ibid*, **53**, 224 (1905) THIS JOURNAL **27**, 144 (1905) *Proc Am Pharm Assoc* **56**, 805 (1908) *Ibid* **57**, 889 (1909) *J Am Pharm Assoc* **1**, 849 (1912)

[4] THIS JOURNAL **27**, 155 (1905)

[5] *Compt rend* **155**, 783 925 (1912)

[6] Unpublished manuscript

All the samples were soluble in all proportions in 90% alcohol.   Samples I and III were soluble in 16 and 25 parts, respectively of 70% alcohol

The specific gravity at 25°/25° was 0 9209, 0 9161, 0 9136

Optical rotation in 100 mm tube was +2 85, +2 84, +6 6

Index of refraction at 26°, 1 4675, 1 4713, 1 4753

Saponification number 12 5, 14 40, 16 6

Saponification number of acetylated oils 75 1, ——, 65 7

Calculated as borneol and bornyl acetate these oils contained 4 37%, 5 04%, 5 81% respectively, of bornyl acetate, while Sample I contained 18 44% free borneol and Sample III 14 46% of free borneol

Tests for Aldehydes and Ketones —With Schiff's reagent and sodium bisulfite, negative results were obtained, but phenylhydrazine, when applied according to the directions of Mulliken[1] produced cloudiness indicating the presence of a ketone   If a ketone is present it occurred in very small amount and is probably one which does not react with sodium bisulfite

Test for Methoxy Compounds —When tested by the Zeisel method all samples gave negative results, showing the absence of compounds containing the methoxyl group.

Identification and Quantitative Estimation of Cineol.

All fractions formed an addition product when treated with iodol This, after recrystallization from benzene, melted at 111° with decomposition.   Assayed by the official Phosphoric Acid Method, Sample I gave 36% of cineol and Sample III 69%   By the Resorcin Method Sample I gave 35% and Sample III 71%.   The great difference in cineol content of the two oils may be explained in part by the fact that oil No I was obtained from older plants and apparently contains a higher percentage of pinene [2]

Examination for Phenol —The oil was first shaken with a weak solution of sodium carbonate in order to remove free acid, then shaken several times with a 2 5% solution of potassium hydroxide, the caustic alkali solutions were extracted with ether to remove unchanged oil, then acidified with dilute sulfuric acid and again extracted with ether   After evaporation of the ether there remained a small amount of a reddish brown substance in which, on standing, a very small amount of a crystalline solid appeared.   This was pressed between filter paper and tested with an alcoholic solution of ferric chloride, which gave a dirty greenish brown color.   When water was added to this a purple color was formed   This is an indication of salicylic acid

Saponification and Fractionation of the Oils —Sample I was boiled an

[1] "Identification of Pure Organic Compounds," Vol I, 134

[2] It seems to be generally considered, however, that the younger the plants the larger the percentage of terpenes   "The Volatile Oils," Gildemeister-Kremers Vol I, p 285

hour on a water bath with an excess of 0.5 N alcoholic solution of potassium hydroxide. The alcohol was then distilled off on a water bath, the residue mixed with water, the oil separated, washed, dried and fractionated three times under a pressure of 3 mm. Table I shows the fractions obtained, with the rotation, index of refraction and density of each.

TABLE I

No of fraction	Boiling temp	$d_{25°}^{25°}$	α_D.	$n_{D27°}$.
1	50-55°	0 9064	+ 3 3°	1 4580
2	55-60°	0 9090	+ 4 1°	1 4585
3	60 80°	0 9203	+ 2 1°	1 4647
4	80-90°	0 9227	+ 9 2°	1 4796
5	90 100°	0 9380	+14 3°	1 4854
6	100-110°	0 9431	+11 7°	1 4895
7	110-120°	0 9401	+ 8 3°	1 4948
8	120-130°	0 9340	+ 4 9°	1 4982
9	130-140°	0 9571	— 1 1°	1 4987

These fractions were then distilled under atmospheric pressure, yielding fractions with the following boiling temperatures

1 155-160°, 2, 160-170°, 3, 170-176°, 4, 176-180°, 5, 180 190°, 6, 190-200°; 7 200-210°, 8, 210-220°, 9, 220-230°, 10, 230-240°

Sample of oil No. III, after removal of phenol, was saponified, then fractionated four times under a pressure of 15 mm. and once under atmospheric pressure. Table II shows the fractions obtained with the rotation, index of refraction and density of each.

TABLE II

No of fraction	Boiling temp	$d_{25°}^{25°}$	α_D.	$n_{D16°}$.
1	160-170°	0 898	+ 5 5°	1 45950
2	170-175°	0 904	+ 4 3°	1 45859
3	175-185°	0 921		1 46429
4	185-200°			1 46806
5	200-210°	0 939	+15 8°	1 47681
6	210-220°	0 943	+17 8°	1 48179
7	220-240°	0 926		1 48711
8	240-260°	0 926	+ 9 95°	1 49668
9	260-273°	0 895	— 4 7°	1 48841

In addition to these fractions, there was obtained from the alcohol which was distilled off from the saponification mixture a small amount of an oil which boiled between 155° and 160°.

Identification of Pinene.—The fraction boiling at 155-160° was treated by the method of P. Ehestädt[1] for the preparation of pinene nitrosyl chloride. The product obtained was purified by dissolving it in chloroform and precipitating by the addition of methyl alcohol. The substance thus obtained melted at 101-102°. A nitrolbenzylamine also was prepared which melted at 122-123°. The preparation of these two com-

[1] *Report of Schimmel & Co*, April, 1910, 164.

pounds may be considered as proof of the presence of pinene. As shown by the optical rotation it is a mixture of dextro- and levo-α-pinene with the dextro- form slightly predominating. The low dextro-rotation may also be accounted for in part by the presence of cineol, which is optically inactive. The index of refraction of the lowest boiling fractions is lower than that of pinene while the density is higher. Both of these points of difference are likewise explained by the presence of cineol.

Identification of Cineol.—The fractions boiling between 170° and 180° in the case of oil No. I, and those boiling between 170° and 185° in the case of oil No. II, were composed chiefly of cineol, as shown by the odor, boiling temperature, density, the iodole test and by the fact that the greater part was dissolved by a 50% solution of resorcin.

Test for Linalool.—Fractions boiling between 180° and 200° were oxidized with chromic acid mixture, the mixture neutralized and distilled with steam. The liquid recovered had a light yellow color and an odor suggesting that of citral. This was treated with semicarbazide hydrochloride according to Zelinsky[1] for the preparation of semicarbazones. The substance obtained was recrystallized from methyl alcohol and the melting point determined. It began to soften at 193° and melted at about 200°. Citral forms two semicarbazones, one melting at 164° and the other at 171-172°. Camphor semicarbazone melts 236-238°. The product obtained in this experiment was probably a mixture of citral semicarbazone and camphor semicarbazone, since borneol was proved to be a constituent of the next higher boiling fraction.

Test for Camphor. Identification of Borneol.—The fractions boiling between 200° and 240° were fractionated again twice, collecting in one fraction all that portion which distilled between 200° and 220°. Some of this was treated with hydroxylamine hydrochloride in the usual manner for the preparation of camphor oxime. The result was negative. The remainder of this fraction was oxidized with Beckmann's chromic acid mixture, the acid neutralized and the mixture distilled with steam. The oil obtained was treated with hydroxylamine hydrochloride. An oxime was obtained which, after recrystallization from diluted alcohol, had the melting point, 118-119°. The melting point of camphor oxime is generally given as 117-119°.

The high boiling portion of the oil was not identified. Judging from the boiling temperature, the index of refraction and the density, it probably consists of one or more sesquiterpenes. As will be seen from Table III

TABLE III.

	Boiling point.	Density.	Rotation	Index of refraction
Caryophyllene . .	258–260°	0 908 at 15°	—8 7°	1 4997 at 20°
Fraction No. 9 . .	260–273°	0 895 at 25°	—4 7°	1 4884 at 26°

[1] *Ber.*, **30**, 1541 (1897)

there is a fair degree of agreement between the physical constants of caryophyllene and those of one of the high boiling fractions of oil No. III.

But an attempt to prepare caryophyllene hydrate resulted negatively. The amount at hand was not sufficient for further tests.

Identification of Acids.

The alkaline liquid resulting from the saponification of oil No. I was evaporated to a small volume, acidified and distilled with steam. The acid distillate was neutralized with sodium hydroxide and precipitated with silver nitrate. Very decided reduction of the silver occurred, indicating the presence of formic acid.

The distillate from oil No. I was neutralized with sodium carbonate and evaporated to a small volume. Oil No. I was shaken with a 2–3% solution of sodium carbonate, the aqueous liquid evaporated to a small volume and mixed with the concentrated distillate, the mixture acidified and distilled with steam. The distillate was neutralized with sodium hydroxide and precipitated with silver nitrate. The dried salt gave upon ignition 50.2% of metallic silver.

The alkaline liquid resulting from the saponification of oil No. III was concentrated, acidified and distilled with steam. The distillate was collected in two portions, neutralized with ammonia and precipitated with silver nitrate. The amount of the first precipitate was very small. The precipitate from the second fraction yielded, upon ignition, 63.66% of metallic silver.

From the portion remaining in the flask a silver compound was prepared which, upon ignition, left a residue of 38.16% of metallic silver.

The silver salts of some of the fatty acids which occur in volatile oils contain the following percentages of silver.

Of acetic acid, 64 64%, butyric acid, 55 34%, valerianic acid, 51 64%, caproic acid, 48 39%, caprylic acid, 42 59%, capric acid, 38 67%

The results obtained indicate therefore that the oils contain formic acid, acetic acid and at least one other (higher) fatty acid.

Summary.

From the foregoing investigation it follows that oil of *Calycanthus floridus* contains the following compounds, the cineol predominating:

1	*d-α*-Pinene	5	Linalöol?
2	*l-α*-Pinene	6	Bornyl acetate
3	Cineol	7	Salicylic acid
4	Borneol	8	One or more esters in addition to bornyl acetate

ALABAMA POLYTECHNIC INSTITUTE,
     AUBURN, ALA

THE HYDROGEN NUMBER OF SOME ESSENTIAL OILS AND ESSENTIAL OIL PRODUCTS. I. OILS OF SASSAFRAS, ANISE, FENNEL, CLOVE AND PIMENTA.

BY ALAN R. ALBRIGHT.
Received August 24, 1914

Introduction.

This paper describes a new method for the examination of certain ethereal oils. It depends on the fact that some unsaturated compounds in such oils are capable of quantitative hydrogenation in a solution of colloidal palladium. S. Fokin[1] suggests a "hydrogen number" for unsaturated aliphatic compounds, using molecular platinum as catalyzer, but states that *no cyclic* unsaturated compound will give this. It has been found that a "hydrogen number," corresponding to the iodine number of fatty oils, may be ascribed to some ethereal oils of the type to be discussed.

Catalyzer.—The colloidal palladium used in this work is a commercial product,[2] but it may not be amiss to describe very briefly its preparation.[3] A solution of a palladium salt is added to a solution of an alkali salt of an acid of high molecular weight, in this case the sodium salt of protalbinic acid (an egg albumin decomposition product). An excess of alkali dissolves the precipitate formed and the solution is said to contain the palladium in the form of a hydrosol of its hydroxide. This solution is purified by dialysis and the hydroxide reduced with hydrazine hydrate. On further dialysis and evaporation to dryness there is obtained a water-soluble product consisting of colloidal palladium and sodium protalbinate in the form of black shining lamellae, which contains about 60% palladium. The sodium protalbinate present in the mixture acts, when the material is in solution, as a "protective colloid."[4]

As is well known, colloids in general are precipitated, "flocked out,"
$$\overset{+\ -}{}$$
by ions (e. g., As_2S_3 by HCl), due to a transfer of electrical charges, but in the presence of a protective colloid relatively large amounts of electrolytes are necessary to bring this about.

Hydrogenation involving the use of colloidal palladium differs from some other processes of catalytic reduction in that the reaction has not been observed to proceed in the absence of water nor if the proportion of water in the reaction mixture be too small. For instance, in the case of

[1] *J. Russ. Phys. Chem. Soc.*, **40**, 700–9 (1908); cf. *Chem. Zentr.*, 1908, II, 2039, also *C. A*, **3**, 1009 (1909).

[2] Prepared by Kalle & Co., Biebrich, am/R. Price about $2.40 per gram. See Paal and Hartman, *Ber.*, **43**, 248–9 (1910).

[3] Paal and Amberger, *Ber.*, **37**, 124 (1904); *Chem. Zentr.*, 1904, I, 572.

[4] Paal and Amberger, *loc. cit.*, see also Skita and Franck, *Ber.*, **44**, 2862 (1911); *Chem. Zentr.*, 1911, II, 173.

cottonseed oil, a portion of this material showed no absorption of hydrogen on being shaken with a small quantity of powdered colloidal palladium. The same result was obtained whether the oil was suspended in .95% alcohol or dissolved in acetone. On adding 15 to 20% of water to the acetone solution, however, reduction took place at a fairly rapid rate. If this more convenient form of colloidal palladium be not available, a substitute may be prepared as needed in the following way:[1] 0.05 g. palladous chloride (the quantity generally used in our experiments), is placed in the shaking flask described below, followed by 50 cc. of 50% alcohol and 1 or 2 cc. of a 1% aqueous solution of gum arabic (the weight of gum used being about one-fourth the weight of the $PdCl_2$). On shaking this mixture in an atmosphere of hydrogen, the chloride is reduced with formation of a black solution of colloidal palladium, which is rendered stable, *i. e.*, "reversible," by the small quantity of the reversible colloid present, gum arabic. While this solution may be substituted for that of the technically prepared substance, it is actually more expensive, as experiments show that 0.02 g. colloidal palladium costing $0.048 is at least as active as 0.05 g. $PdCl_2$, costing $0.075. Paal's colloidal palladium and palladous chloride contain approximately equal percentages of the metal.

Certain substances are regarded as poisonous with respect to colloidal palladium, for example, formaldehyde contained in impure methyl alcohol is said to be harmful, and allyl isothiocyanate entirely inactivates it, so that mustard oil, although theoretically coming within the category of available experimental material, cannot be treated.

No attempt is made to isolate either the colloidal palladium as such, or the hydrogenated sample, but the palladium may be recovered by evaporating the reaction mixture to dryness, igniting, converting the metal into the chloride and boiling the solution of this to obtain palladous chloride, which may be used in place of colloidal palladium as previously described.

Apparatus.—The apparatus used in this laboratory, which is shown in Figs. 1 and 2, is similar in principle to that devised in the organic laboratory of the University of Göttingen. Its fundamental parts are the camshaft, carrying four eccentrics; the shaking baskets "A," attached to the cams and suspended from pulleys on a supporting rod; the absorption flasks

Fig. 1.

"B," which are placed in the wire baskets; the gas buret connected
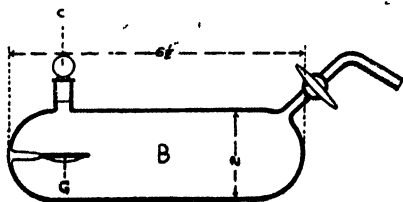
[1] Skita and Franck, *loc. cit.*

by means of a T tube both with the source of hydrogen and with the absorption flask. Power is supplied by a one-eighth h. p. motor belted to. the cam-shaft. When in operation, the shaft has a speed of about 200 revolutions per minute. Hydrogen is supplied from a Kipp generator, or from a steel cylinder and is purified by being passed through a large wash bottle containing alkaline saturated permanganate and is washed with water at each gas buret by a separate wash bottle.

Manipulation.—The manipulation of a reduction is as follows: The air is first displaced from the entire apparatus by passing through it a current of hydrogen, after removing the stopper "C," and lowering the reservoir "D," so that sufficient water remains to form an air trap at the lower bend of the buret. The levels in both arms of the U tube are then equalized at the zero mark. The three-way stopcock "E," is then closed, the stopper "C," which had been replaced during the flushing of the buret
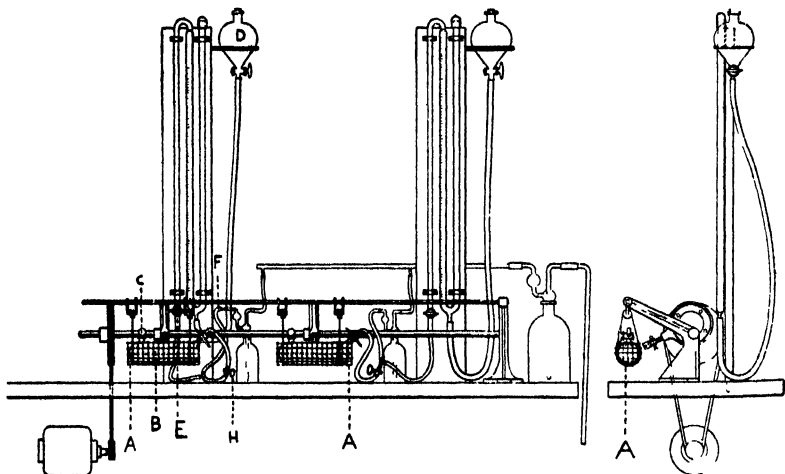
Fig. 2.

with hydrogen, is removed, and 0.02 g. dry colloidal palladium introduced while a current of hydrogen is passing through. Then 50 cc. of 50% alcohol are added, the stopper replaced, the stopcock "F," closed (shown only in photograph) the three-way cock "E," momentarily opened to the air to equalize the pressure in the apparatus with that of the atmosphere, and the flask shaken until no more hydrogen is absorbed. In this way the errors due to (1) absorption of hydrogen by the catalyzer, (2) solubility of the gas in the solvent, and (3) consumption of hydrogen by oxygen dissolved in the solvent, are removed from consideration. The

Fig. 3.
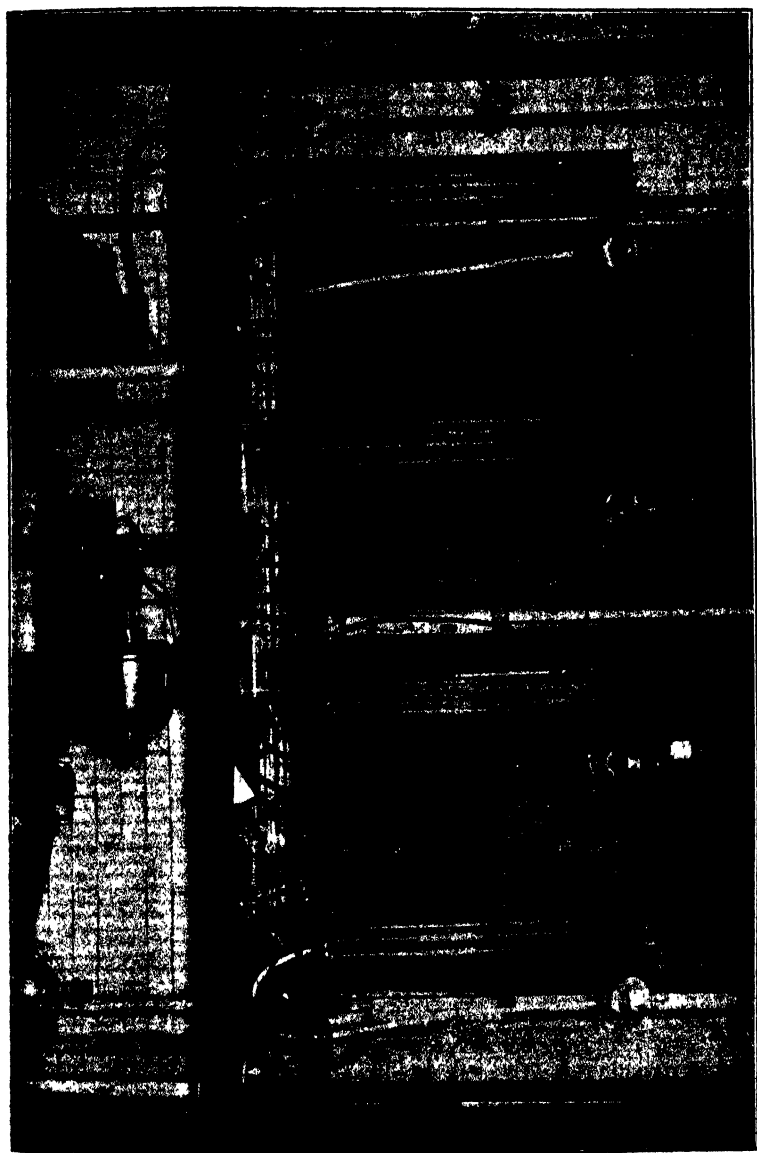
buret is again filled to the zero mark with hydrogen and the shaking flask tilted until the palladium solution has drained from the concave "substance table" "G." The substance under investigation is dropped into this table from an oil pipet (weighing bottle),[1] again preventing the entrance of air by maintaining a current of hydrogen through the apparatus. The purpose of this "substance table" is to prevent contact between the catalyzer and substance under examination until the operator is ready to start the experiment. The stopper "C," is replaced, the cock "F," is closed and the cock "E," opened momentarily to the air again. Connection is then made by the same stopcock between the shaking flask and the buret and the machine is at once set in motion. The absorption of hydrogen is carefully watched, maintaining the same water level in each side of the buret by regulating the flow of water from the reservoir. When the reaction is finished, a decided and abrupt decrease in the rate of absorption occurs. On the accuracy of the observation of this point depends the accuracy of the determination   The end point may readily be found otherwise by noting the buret reading at frequent intervals, e. g., every 15 seconds, and plotting volume against time on coördinate paper, when the break in the resulting curve will give the desired result. This point was found in each of the cases to be described by drawing a straight line through the first points, then connecting with a smooth curve those points which lie at the right. The juncture of the straight line representing the main reaction, with the curved line representing absorption of hydrogen by secondary substances, is taken as the end point. The sample weight should be so adjusted that 100 cc. or less of hydrogen will be needed, but in case more than one buret of the gas is to be absorbed, the procedure is as follows: First, the reading is noted and the clamp "H," closed (without interrupting the shaking); then the reservoir is lowered and the cock "F," opened until the water in the graduated branch of the U tube is forced by the pressure of hydrogen from the cylinder down to the level of that in the other and then closed, again reading the buret. The reservoir is hung in the hook, an amount of water equal to about twice the quant of hydrogen which has been absorbed during the time of refilling the bu (roughly calculated from the previously observed rate of absorption) allowed to enter the right arm, and the partial vacuum which has been formed in the shaking flask is released when the clamp "H," is opened. The levels in the two arms of the buret are equalized and the absorption continued to completion.

Application.—Every essential oil contains at least small quantities of unsaturated substances, consisting, for example, of one or more terpenes, such as limonene, or phellandrene,

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[1] Devised by H. S. Bailey of this laboratory.
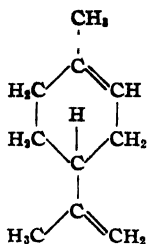
Limonene
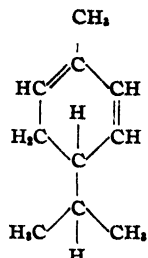
Phellandrene (α)

and theoretically a measure of the total "degree of unsaturation" might present a factor useful in judging the purity of the product. Not all double bonds, however, are hydrogenated with equal ease, owing to effects of molecular configuration, and some are only very slowly attacked by activated hydrogen. For example, limonene is first reduced to carvomenthene,[1] citral to citronellal,[2] carvoxime to carvotanacetoxime,[3] the
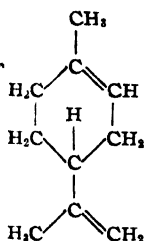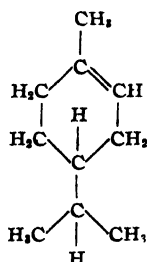
Limonene   Carvomenthene   Citral   Citronellal.
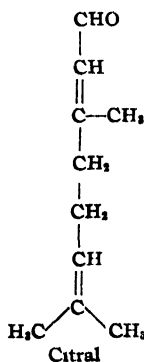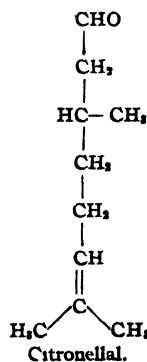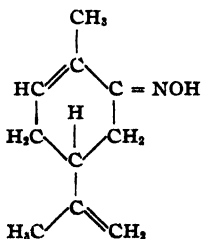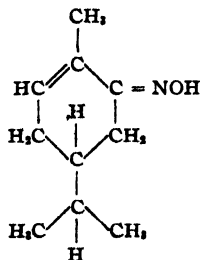
Carvoxime   Carvotanacetoxime

[1] With Pt black as catalyzer, Vavon, *Chem Zentr*, 1914, I, 1506, with CuO as catalyzer Ipatieff, *C A*, 5, 891 (1911)

[2] Skita, *Ber*, 42, 1627 (1909), cf *Chem Zentr*, 1909, I, 1931; also *C A*, 3, 2159 (1909)

[3] Albright, "Inaugural Dissertation," Göttingen, 1912; Wallach and Albright, *Ann*, 403, 73 (1914)

second bond in each case requiring considerably longer treatment for complete saturation.

Thus it is seen that the application of a quantitative method in such cases may be attended by unsatisfactory results, in that far too much time may be required for a determination, with possible attendant errors of changing atmospheric temperature and pressure.

Some oils, however, contain compounds which are completely and very rapidly reduced, and it is with oils of this type that the present paper deals. Most notable are those containing a constituent which has within its molecule an allyl or propenyl group, as the double bonds in such groupings are generally capable of very rapid hydrogenation. (Allyl isothiocyanate mentioned before is an exception.) In fact, some compounds of this type are so rapidly reduced that, when an oil containing one of them is under examination, the reaction seems to take a selective course, in that these bonds are quantitatively saturated before those in other configurations are attacked to more than a slight extent. As a matter of fact, however, the reaction is not to be considered rigidly selective, and it is in this fact that the principal error of the determination lies. Nevertheless, in most cases the change in velocity of hydrogen absorption, after the allyl or propenyl group has been saturated, is sufficiently abrupt so that there is no mistaking the end point of the reaction. It is the quantity of hydrogen absorbed in this first and most vigorous action that fixes the "hydrogen number" of the oil. In other words, the hydrogen number of an oil is the number of cc. of hydrogen, reduced to the volume it would occupy at $0°$ and 760 mm. pressure, which are absorbed by 1 g. of the material in question *during the above described period of most rapid absorption of the gas.* This quantity has been found to be characteristic of the several oils named, and gives a direct measure of the proportion of the active constituent present. For example, from the hydrogen number of clove oil the percentage of eugenol may be readily calculated by multiplying by the factor 0.0073, the weight of eugenol equivalent to 1 cc. of hydrogen. The results are generally slightly too high because of the absorption of hydrogen by secondary substances in addition to that due to the main reaction. By using an appropriate factor weight the buret reading, reduced to standard conditions, will give the percentage direct of these substances, of course with the same qualification regarding error.

The method of procedure in the working out of the hydrogen number and of the estimation of the principal constituents of the oils under consideration was as follows: first, the active constituents of the oils, namely, safrol, anethol, and eugenol, were prepared in as pure a condition as possible and hydrogenated, in order to prove that they may be quantitatively reduced, and that the break in the curve showing the absorption rate, which is apparently a straight line during the main reaction, actually

represents the complete saturation of the one active double bond in each compound   Then an imitation oil was prepared, made up of the active constituent mentioned, in the approximate proportion in which it occurs in the natural oil, while the remaining percentage was represented by pure limonene   Limonene itself absorbs hydrogen fairly rapidly, and was chosen from among other terpenes for that reason, so that as severe a test as possible might be made   Finally, samples of commercial oils were subjected to the same process

Experimental.

The Reduction of Safrol   A commercial sample of safrol was redistilled, b p 760 mm , 236 0° (mercury entirely in vapor)   This substance is reduced to dihydrosafrol with extreme ease   The speed of reaction and sharpness of the end point are remarkable   One tenth gram colloidal palladium dissolved in about 40 cc 50% alcohol was saturated with hydrogen, then 4 63 g safrol were introduced   Absorption began as soon as agitation was commenced, proceeded at a constant rate and ended very abruptly   In ten minutes 720 cc of hydrogen measured at 22° and

Safrol

Dihydrosafrol

Anethol

Dihydroanethol

Eugenol

Dihydroeugenol
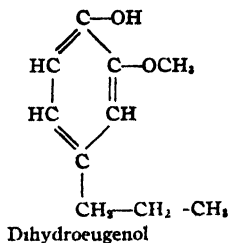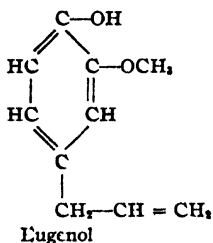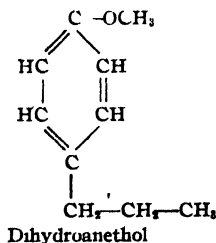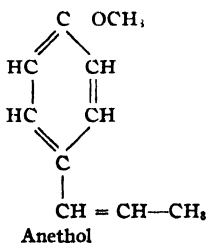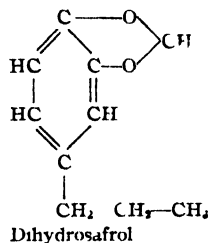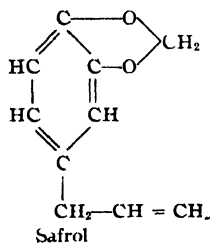
758 mm. had been absorbed. This is equivalent to 632 cc. at 0° and 760 mm., whereas 4.63 g. safrol should theoretically absorb 641 cc. The reaction product was isolated by distilling with steam, dried with fused calcium chloride and distilled under ordinary pressure, b. p., 234.3–234.5° (mercury entirely in vapor).

o 2026 g of substance gave o 1375 g H₂O and o 5461 g CO₂

Calculated for C₁₀H₁₂O₂· H = 7 3, C = 73 2, found 7 6, 73 5.

Specific gravity 15 6°/15 6° = 1 0759, n_D 15 6° = 1 5228, M R = 46 60, calculated = 46 1

Dihydrosafrol is a colorless oil, stable several minutes toward dilute alcoholic permanganate; quite stable toward dilute aqueous permanganate. The odor is very similar to that of safrol.

Since the work upon which this paper is based was begun, there has appeared an article by Ipatieff[1] in which are described the reductions of anethol, eugenol, and safrol with nickel and hydrogen under about 50 atm. pressure and at from 92° to 95°. The preparation of reduction products for the purpose of analysis has been limited to safrol, since the author's results agree with those of Ipatieff, and since there is every reason, from theoretical and experimental considerations, to assume that the reactions, in the case of anethol and of eugenol, proceed normally as indicated in the above formulas.
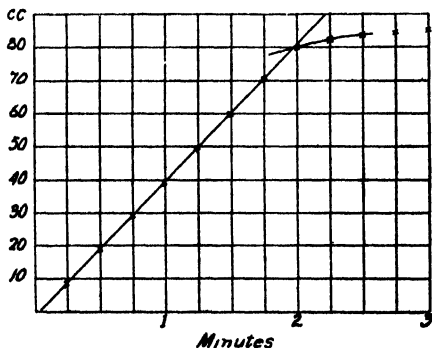
Fig. 4 —Safrol.

Fig. 4 gives a typical curve showing the rate of absorption of hydrogen by safrol. The raw material was a sample of commercial safrol, "Pure U. S. P"

This was frozen and pressed out, then distilled under 763 mm. pressure, b. p., 236.3–236.6° (mercury entirely in vapor).

As described before, 0.02 g. colloidal palladium with 50 cc. 50% alcohol were saturated with hydrogen in the shaking flask, after which 0.5119 g. of the substance was introduced. The hydrogen was measured at 24.5°, 766.5 mm. The break in the curve occurs at 80.0 cc., equivalent at 0°, 760 mm. to 69.4 cc., whereas the theoretical absorption is 70 7 cc. Hydrogen number, 135.6; safrol = 98.3%. Each of a number of reductions of safrol gave a result 1 to 2% too low, indicating the probable presence of some much less active substance difficult to separate from safrol.

Fig. 5 shows the rate of absorption of hydrogen by pure limonene from

[1] *Ber*, **46**, 3589 (1913), cf. *Chem Zentr*, 1914, I, 140

lemon oils, redistilled several times over sodium   The catalytic reagent consisted, as in each of the cases to be described, of 0 02 g colloidal pal ladium in 50 cc 50% alcohol   The sample weighed 0 0390 g and the gas was measured at 25°, 766 mm

Fig 5 —Limonene

Fig 6 represents the reduction of a factitious sassafras oil, a mixture of 4 000 g redistilled commercial safrol and 1 000 g limonene   The quantity taken was 0 561 g and the break in the absorption curve occurred at 73 7 cc measured at 26 5°, 765 5 mm   At 0°, 760 mm this is equivalent to 62 8 cc giving a hydrogen number of 111 9   Eighty per cent of 0 561 g or 0 449 g safrol at 0°, 760 mm should absorb 62 2 cc , the error being due pri marily to the 20% of limonene present   The proportion of safrol calculated from the absorption is 81 1%

Fig 7 represents the hydrogena tion of an authentic sassafras oil Curve 1 gives the result obtained using 0 4261 g oil, Curve 2 using 0 5071 g No 1 absorbed 51 0 cc , No 2 60 0 cc , each measured at 25°, 763 4 mm   At 0°, 760 mm , absorption by No 1 would have been 43 9 cc , giving a hydrogen number of 103 1, and a safrol con tent of 74 8%, by No 2, 51 7 cc ,
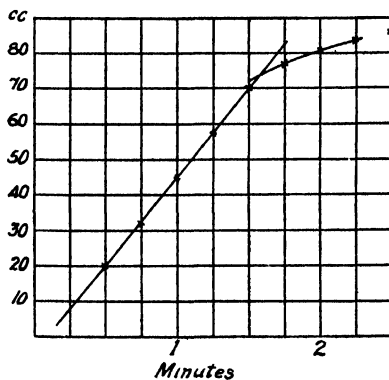
Fig 6 —Imitation Sassafras Oil

giving 102 0 as the hydrogen number, and 74 0% as the safrol content

Fig 8 shows the course of a reduction of pure anethol, prepared by freezing and pressing out a sample of commercial anethol   The quantity taken was 0 4417 g , the sharp break in the absorption curve coming at 79 2 cc measured at 28°, 762 4 mm   This is equivalent at 0°, 760 mm to 66 5 cc   Theory requires an absorption of 66 8 cc at 0°, 760 mm   Hy drogen number, 150 5   anethol = 99 6%

Fig 9 represents the reduction of an imitation anise oil, made of 8 000 g pure anethol and 2 000 g pure limonene   No 1 shows the result obtained with 0 4180 g of the mixture   The break occurs at 61 cc measured at 24 5°, 759 mm   This is equivalent at 0°, 760 mm to 52 3 cc , giving a hydrogen number of 125 1, and an anethol content in the oil of 82 4% For No 2, 0 3220 g was taken   The break is at 47 5 cc measured under

the same conditions as for No. 1, equivalent at 0°, 760 mm., to 40.9 cc. Hydrogen number, 127.0; anethol = 83.7%.
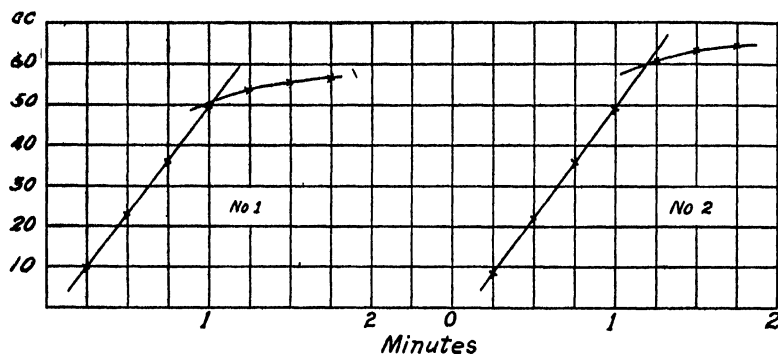
Fig. 7 —Authentic Sassafras Oil.

Fig. 10 shows the results obtained with a commercial anise oil. For No. 1, 0.4109 g. was taken. The end point is at 61.1 cc. measured at 26°, 756 mm., equivalent to 51.7 cc. at 0°, 760 mm., giving 125.8 as the hydrogen number, and 82.9% as the anethol content. For No. 2, 0.4019 g. oil was used, the end point occurring at 60.6 cc. measured under the same conditions as No. 1, equivalent to 51.2 cc. at 0°, 760 mm. Hydrogen number, 127.3; anethol = 83.9%.
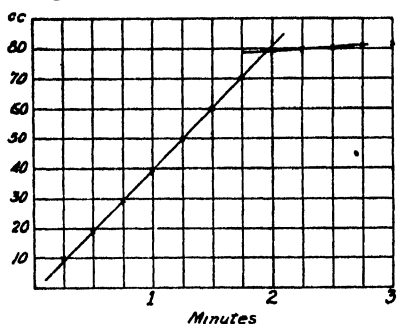
Fig. 8.—Anethol.

Fig. 11. A representative commercial fennel oil. No 1. 0.5378 g. absorbed 62.0 cc. at 22°, 764.4 mm.,
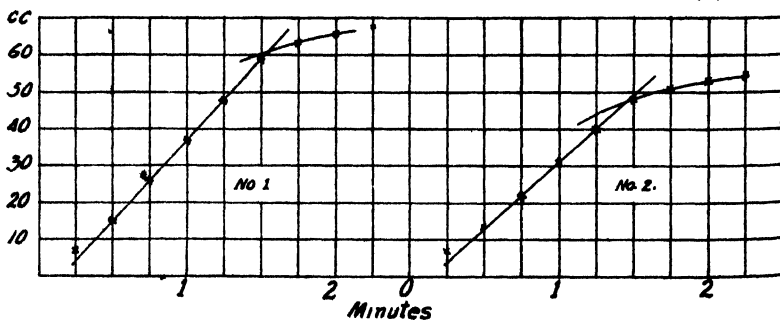
Fig 9 —Imitation Anise Oil
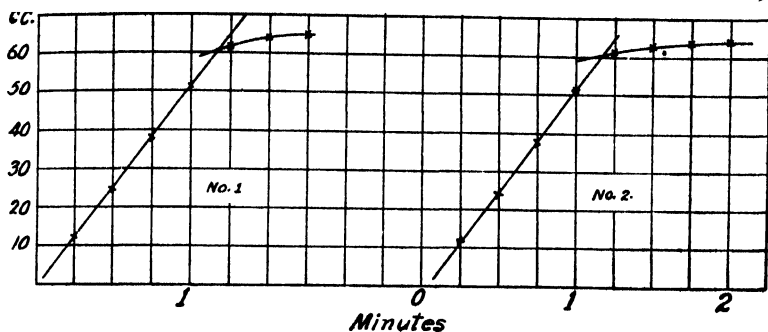
Fig. 10.—Commercial Anise Oil.
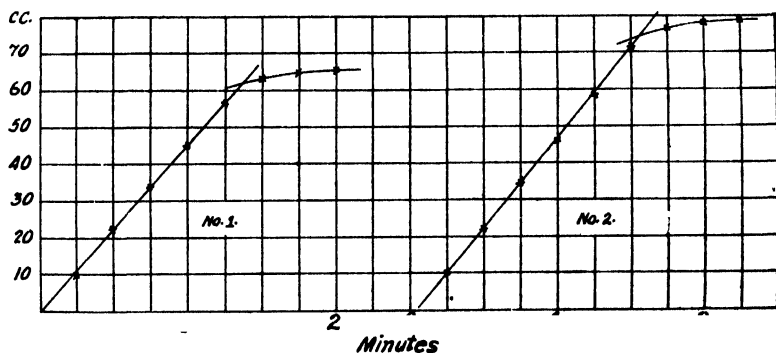
Fig. 11.—Commercial Fennel Oil.

equivalent to 54.4 cc. at 0°, 706 mm., giving 101.3 as the hydrogen number, which represents 66.8% anethol.   No. 2: 0.6330 g. at 23°, 764.4 mm., absorbed 74.5 cc., equivalent to 65.0 cc. at 0°. 760 mm.   Hydrogen number, 102.7; anethol = 67.7%.

Fig. 12 represents a reduction of eugenol.   The raw mateiial was a commercial eugenol, "Pure U.S. P."   It was redistilled, b. p., 13 mm., 150–152° (uncor.).   0.4769 g. absorbed 77.7 cc. at 30°, 762.7 mm., equivalent to 64.1 cc. at 0°, 760 mm.   Theoretical absorption, 65.1 cc.   Hydrogen number, 134.4; eugenol = 98.3%.
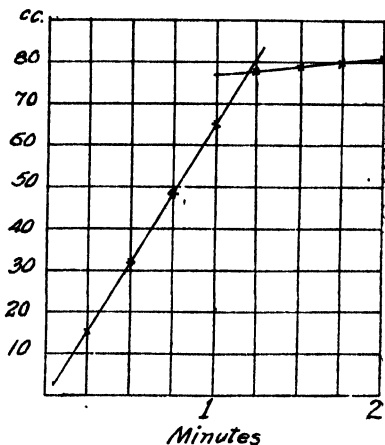
Fig. 12 — Eugenol
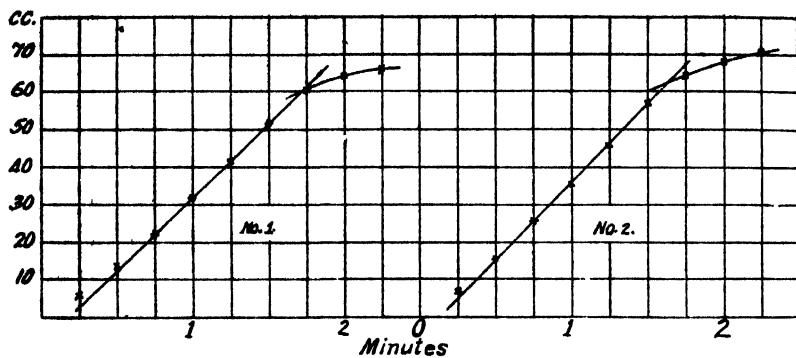
Fig. 13.—Imitation Clove Oil
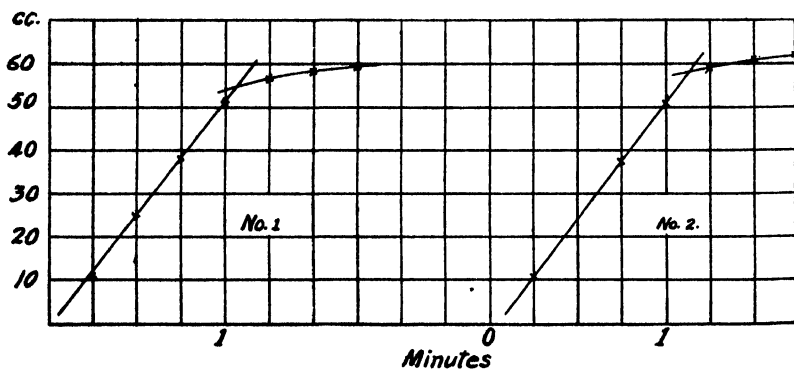
Fig. 14.—Commercial Clove Oil.
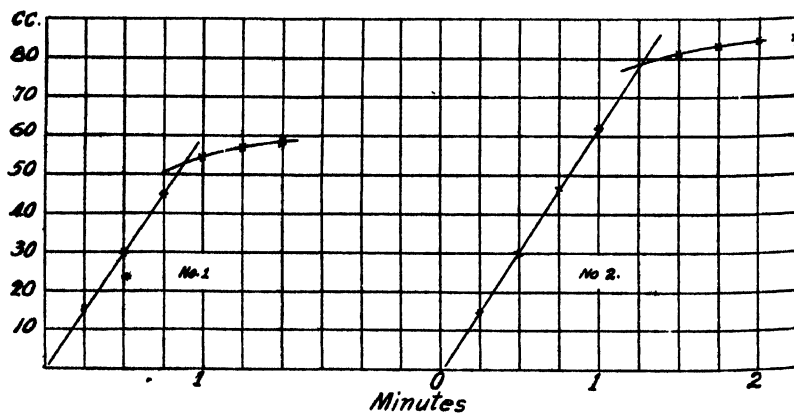
Fig. 15.—Commercial Pimenta Oil.

Fig. 13 shows results obtained on hydrogenating a mixture of 8.000 g. redistilled eugenol and 2.000 g. limonene. No. 1: 0.4620 g. absorbed 60 2 cc. at 24°, 765 mm., equivalent to 52.3 cc. at 0°, 760 mm. Hydrogen number, 113.2; eugenol = 82.8%. No. 2: 0.4806 g. absorbed 62.8 cc. under the same conditions, equivalent to 54.5 cc. at 0°, 760 mm., giving 113.3 as the hydrogen number, which represents 82.8% eugenol.

Fig. 14 shows the results of two experiments with a commercial clove oil. For No. 1, 0.4104 g. was taken, which absorbed 55.0 cc. at 26°, 763 mm., equivalent to 47.0 cc. at 0°, 760 mm. Hydrogen number, 114.6; eugenol = 83.8%. For No. 2, 0.4339 g. oil was used. The absorption at 27°, 763 mm. was 58.3 cc., equivalent to 49.5 cc. at 0°, 760 mm. Hydrogen number, 114.0, eugenol = 83.3%.

Fig. 15 represents reductions of pimenta oil. For No. 1, 0.4592 g. of a representative commercial oil was taken, which absorbed at 27°, 763 mm., 53.0 cc., equivalent to 44.9 cc. at 0°, 760 mm. Hydrogen number, 97.8, eugenol = 71.5%. For No. 2, 0.6830 g. of the same oil was used. Under the same experimental conditions there were absorbed 78.7 cc., equivalent to 66.8 cc. at 0°, 760 mm. Hydrogen number, 97.8; eugenol = 71.5%.

The values for the vapor pressure of the solvent (50% alcohol), used in calculating these results were interpolated between figures published by Doroschewski,[1] and are given in Table I.

TABLE I.

Temperature	V p 50% alcohol in mm. mercury	Temperature	V. p
22 0	42 7	26 0	52 5
22 5	43 8	26 5	54 0
23 0	45 0	27 0	55 5
23 5	46 2	27 5	57 0
24 0	47 4	28 0	58.8
24 5	48 5	28 5	60 5
25 0	49 7	29 0	62 6
25 5	50 9	29 5	64 4
		30 0	66 8

Experiments carried out in this laboratory indicate that the effect of either the catalyzer or oil upon the vapor pressure of the alcohol is negligible.

The results of the above described experiments are given in Table II.

It is planned to obtain a number of additional authentic samples of these and of other oils, so that this table may be amplified and limits for the hydrogen numbers set. It is further our intention to adapt the method to those materials which at present seem to offer greater difficulty, and to devise a simpler and less expensive form of apparatus which may aid the method in finding commercial application.

[1] *Z. physik Chem.*, **73**, 192 (1910).

TABLE II

Figure	Substance	Hydrogen number	Per cent of active constituent	Theoretical per cent of active constituent
3	Safrol	135 6	98 3	100 0
4	Limonene			
5	Imitation sassafras oil	111 9	81 1	80 0
6	Authentic sassafras oil	103 1	74 8	
		102 0	74 0	
7	Anethol	150 5	99 6	100 0
8	Imitation anise oil	125 1	82 4	80 0
		127 0	83 7	80 0
9	Commercial anise oil	125 8	82 9	
		127 3	83 9	
10	Commercial fennel oil	101 3	66 8	
		102 7	67 7	
11	Eugenol	134 4	98 3	100 0
12	Imitation clove oil	113 2	82 8	80 0
		113 3	82 8	80 0
13	Commercial clove oil	114 6	83 8	
		114 0	83 3	
14	Commercial pimenta oil	97 8	71 5	
		97 8	71 5	

WASHINGTON D C

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI [

THREE ISOMERIC ETHYL SECONDARYBUTYL HYDROXYL-AMINES.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER
Received July 31 1914

By the substitution of two different groups for hydrogen in hydroxyl-amine, three isomeric compounds are possible and may be represented by the following general formulas
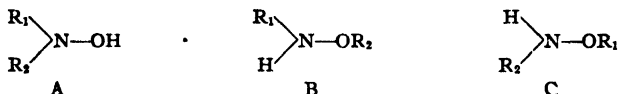
Compounds of the type A, β,β-derivatives,[1] were first prepared by Bewad.[2] The first representative of types B and C, α,β-derivatives, was the α-benzyl-β-ethyl derivative prepared by Behrend and Leuchs[3] in 1890. Since then no compounds of the α,β type containing two different radicals were described until Jones,[4] in 1907, prepared two isomeric compounds, viz, α ethyl β-methyl and α-methyl β ethyl hydroxylamines

It is the purpose of the present paper to describe the preparation and properties of two new α,β-dialkyl hydroxylamines, which are isomeric

[1] In this paper α = attached to O β = attached to N
[2] Bewad Ber [1] 479 (1888) J russ phys Chem Soc 32, 420 (1900)
[3] Behrend and Leuchs Ann 257, 237 (1890)
[4] Jones Am Chem J 38, 253 (1907)

with the first dialkyl hydroxylamine prepared by Bewad, namely, β-ethyl-β-secondarybutyl hydroxylamine The following formulas represent the three isomers

$$C_2H_5 \diagdown$$
$$\qquad N\text{—}OH$$
$$CH_3\text{—}C \diagup$$
$$H \quad C_2H_5$$
I

$$sec\ C_4H_9 \diagdown$$
$$\qquad N\text{—}OC_2H_5$$
$$H \diagup$$
II

$$C_2H_5 \diagdown$$
$$\qquad N\text{—} O \quad C_4H_9\ sec$$
$$H \diagup$$
III
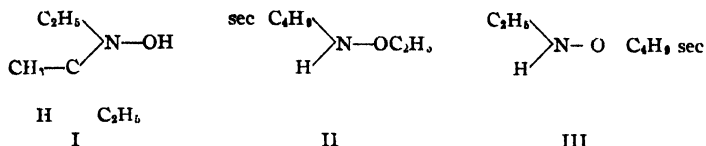
Historical.

I β-Ethyl β-Secondarybutyl Hydroxylamine   In an article on the action of zinc ethyl on nitro compounds of the fatty series and on their bromo derivatives published in 1888,[1] Bewad described, what he believed to be, triethyl hydroxylamine obtained by the action of zinc ethyl on nitroethane   In this first stage of the reaction he obtained a crystalline compound which he assumed to have the formula $2C_2H_5NO_2 + Zn(C_2H_5)_2$ The subsequent disappearance of these crystals was explained by the formation of $(C_2H_5)_3N(OZnC_2H_5)_2$ which interacted with water to give the hydrate of triethyl hydroxylamine,

$$(C_2H_5)_3N(OZnC_2H_5)_2 + 4H_2O = (C_2H_5)_3N(OH)_2 + 2C_2H_6 + 2Zn(OH)_2$$

He assumed that the hydrate lost water, leaving triethyl hydroxylamine, $(C_2H_5)_3N = O$ Upon reducing the supposed triethyl hydroxylamine, Bewad believed he obtained triethyl amine, and, therefore, arrived at the conclusion that the action of zinc alkyls on nitroparaffins was a means of preparing trialkyl hydroxylamines

In 1899, Dunstan and Goulding[2] showed that by the action of ethyl iodide upon diethyl hydroxylamine, triethyl oxamine was produced They gave an account of its reactions and showed it to be a true oxamine, $(C_2H_5)_3N = O$, and not the isomeric triethyl hydroxylamine $(C_2H_5)_2NOC_2H_5$ They later obtained the same compound by the direct oxidation of triethylamine with hydrogen peroxide Bewad had given his compound the formula $(C_2H_5)_3N = O$, on account of its having furnished, as he believed, triethylamine upon reduction   But the properties of Bewad's compound differed so markedly from those of the compound described by Dunstan and Goulding, it was considered possible that Bewad had obtained the isomeric triethyl hydroxylamine, $(C_2H_5)_2N\text{—}OC_2H_5$, and not the oxamine   But the properties of the compound described by Bewad were not such as would be expected from a substituted hydroxylamine of the formula $(C_2H_5)_2NOC_2H_5$

In 1900, Lachman[3] prepared β-diethyl hydroxylamine by the action

[1] Bewad *J Russ Phys Chem Soc* **1**, 125 (1888)
[2] Dunstan and Goulding *Trans J Chem Soc* **75**, 792 (1899)
[3] Lachman *Ber* **33**, 1022 (1900)

of zinc ethyl on diphenyl nitrosamine, and found the product to be identical with the one obtained by Dunstan and Goulding from ethyl iodide and hydroxylamine. The identity of these two compounds, and the isomerism existing between the triethyl oxamine of Bewad and of Dunstan and Goulding led Lachman to compare the properties of the two triethyl oxamines obtained by the two methods. He, too, concluded that Bewad's compound had not the same properties as Dunstan's and Goulding's triethyl hydroxylamine. Lachman, to investigate the problem further, prepared a compound by the action of methyl iodide upon Bewad's so-called triethyl oxamine and assigned to it the formula $(C_2H_5)_3NOCH_3I$, having concluded that it underwent decomposition into formaldehyde and triethyl amine. This, however, did not agree with the conclusion he had previously reached, that Bewad's compound was not identical with Dunstan's and Goulding's.

It was soon shown that the properties Lachman had assigned to his methyl iodide derivative were not correct. Almost simultaneously, Bewad[1] and Dunstan and Goulding[2] arrived at the conclusion that Bewad's supposed triethyl hydroxylamine was β-ethyl-β-secondary butyl hydroxylamine, and the formula $C_2H_5(CH_3)CHN(C_2H_5)OH$ satisfactorily accounted for its properties. Bewad described a general method for the preparation of β-dialkyl hydroxylamines by the action of zinc alkyls on primary or secondary nitroparaffins. The β-dialkyl hydroxylamines obtained in this way were identical with the ones prepared by Dunstan and Goulding by the action of alkyl iodides upon hydroxylamine.

In the preparation of the α,β-compounds containing the same two alkyl groups as Bewad's β,β compound, the method described by Jones in the preparation of two isomeric α,β-methyl ethyl hydroxylamines was followed.[3] Two different alkyl groups were introduced successively into hydroxyurethane, and the resulting product hydrolyzed. To prepare the mono-substituted hydroxyurethane, an alcoholic solution of hydroxyurethane was mixed with a theoretical quantity of alkyl halide, and treated with the calculated amount of potassium hydroxide dissolved in alcohol. The potassium iodide which separated was filtered off, and the solution extracted with ether. In the work of Jones, and in the later work of Hecker[4] the ether solution was found to contain a mixture of the mono- and dialkyl esters of hydroxyurethane. These two products were separated by shaking the ether solution with dilute alkalies, whereby the salt of the mono-alkyl[4] compound dissolved in water, and the di-compound remained in the ether solution. But in the preparation of the second-

[1] Bewad, *J Russ Chem Soc.*, **32**, 420 (1900)

[2] Dunstan and Goulding, *J. Chem Soc*, **79**, 641 (1901)

[3] Jones, *Am Chem J*, **38**, 253 (1907).

[4] Hecker, *Ibid*, **50**, 444 (1913)

arybutyl hydroxyurethane no di-derivative was formed. This was shown by extracting with dilute alkali, and fractionating the ether solution which was left. Only a few drops of an oil were obtained and these gave an analysis agreeing with that for the mono-compound

To prepare the α,β-dialkyl derivatives, equivalent quantities of the monoalkyl hydroxyurethane and of alkyliodide were treated with the theoretical amount of sodium ethylate in alcohol The α,β-dialkyl derivatives of hydroxyurethane were converted into their corresponding hydroxylamines by heating them with an excess of potassium hydroxide solution in sealed tubes, at a temperature below 100° The product was distilled into dilute hydrochloric acid, and the resulting chloride decomposed with solid potassium hydroxide

The hydroxyurethane used in the following work was prepared according to the method described by Jones [1]

Experimental Part.

II The Preparation of α Ethyl β Secondarybutyl Hydroxylamine

The α-ethyl hydroxyurethane used was prepared according to the method described by Jones [2]

(a) *α-Ethyl β-Secondarybutyl Hydroxyurethane,* $\begin{array}{l} O \quad C{-}OC_2H_5 \\ \qquad | \\ C_4H_9{-}N{-}OC_2H_5 \end{array}$ —
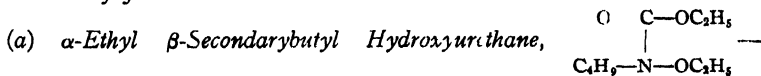
Thirty grams of secondarybutyl iodide and 23 g of α-ethyl hydroxyurethane were mixed with a quantitative amount of sodium ethylate and enough absolute alcohol to make a homogeneous mixture When the mixture was allowed to stand at room temperature for five days, a slight precipitate formed The contents of the flask were then heated on a water bath for 3 hrs A heavy precipitate of sodium iodide was formed and was filtered off After most of the alcohol was removed by distillation, the solution was diluted with water and extracted repeatedly with ether Traces of iodine were removed with sodium thiosulfate and the ether solution was dried with sodium sulfate The ether was removed by distillation and the residue fractionated under diminished pressure Upon analysis, the colorless oil which was obtained was found to contain more nitrogen than was required by theory The oil was found to contain a small amount of unconverted hydroxyurethane which was readily removed by shaking it with sodium hydroxide solution After drying the oil and fractionating it again, 10 2 g of a colorless liquid with a peculiar, rather pleasant odor were obtained. It boiled at 105–106 4° under 55 mm pressure, was only slightly soluble in water, but readily soluble in alcohol and in ether

Calc for $C_9H_{19}O_3N$ N, 7 41 found 7 9

[1] Jones, *Am Chem J*, **20**, 41 (1898)
[2] Jones, *Loc cit*

(b) *α-Ethyl β-Secondarybutyl Hydroxylammonium Chloride*, $\overset{\overset{\displaystyle H}{|}}{\underset{\overset{\diagup\diagdown}{Cl\quad C_4H_9}}{H-N-OC_2H_5}}$.
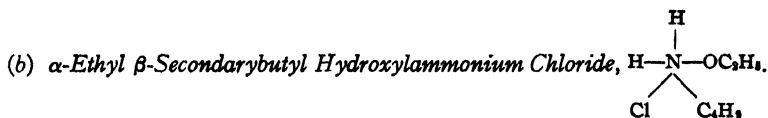
—Five grams of α-ethyl β-secondarybutyl hydroxyurethane were mixed with a water solution containing 7 g. of potassium hydroxide and heated in a sealed tube from 95–100°, for 36 hrs. The contents of the tube were distilled into a dilute solution of hydrochloric acid. The acid solution was evaporated to the consistency of a thick oil and was then transferred to a vacuum desiccator. When the last traces of liquid were removed, a colorless crystalline solid, somewhat deliquescent, remained. This was purified by dissolving in absolute alcohol and reprecipitating it with dry ether. Its melting point was 94°. 1.9 g. were obtained. The chloroplatinate was precipitated as a yellow well defined crystalline solid, by mixing an alcoholic solution of the hydrochloride with an alcoholic solution of platinic chloride, and adding an excess of dry ether.

Calc for $C_{12}H_{12}O_2NPtCl_6$ Pt, 30 30, found 30 07.

(c) *α-Ethyl β-Secondarybutyl Hydroxylamine*, $\overset{\displaystyle H-N-OC_2H_5}{\underset{\displaystyle C_4H_9}{|}}$.—One and
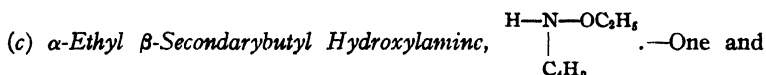
five-tenths grams of the chloride were placed in a distilling flask and covered with an excess of powdered potassium hydroxide. Action began at once, and, upon application of gentle heat, a colorless liquid with a faint but distinct ammoniacal odor and boiling at 88.4–89° was obtained.

Calculated for $C_6H_{15}ON$ N, 11 96, found 11 76.

III. The Preparation of α-Secondarybutyl β-Ethyl Hydroxylamine.

(a) *α-Secondarybutyl Hydroxyurethane*, $\overset{\displaystyle O=C-OC_2H_5}{\underset{\displaystyle H-N-OC_4H_9}{|}}$.—An alcoholic

solution containing 100 g. of secondarybutyl iodide, 57 g. of hydroxyurethane and 30.4 g. of potassium hydroxide were allowed to stand for several days and then was heated for two hours on a water bath. The precipitate of potassium iodide which separated was filtered off and the excess of alcohol removed by distillation. Water was added and the solution extracted repeatedly with ether. The ether solution was extracted with a calculated amount of potassium hydroxide solution, a solution of the potassium salt of α-secondarybutyl hydroxyurethane being thereby obtained.

The free ester was obtained by acidifying the solution with 10% sulfuric acid, extracting it with ether, after removing traces of iodine, drying, and fractionating. The fractionation was carried out under diminished pressure, as the ester decomposed at atmospheric pressure. Before

a satisfactory analysis could be made, it was necessary to remove traces of oxyurethane by shaking the oil with sodium hydroxide solution.

Thirty-four grams of a colorless oil, with a peculiar, rather unpleasant odor, slightly soluble in water, and boiling at 116 116.6° at 27 mm., were obtained.

Calculated for $C_7H_{15}O_3N$ N, 8 69, found 8 88

(b) *α-Secondarybutyl β-Ethyl Hydroxyurethane,* $\begin{array}{c} O = C - OC_2H_5 \\ | \\ C_2H_5 - N - OC_4H_9 \end{array}$.—
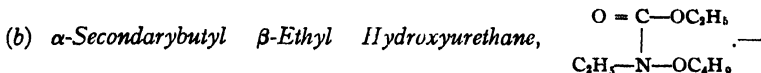
A mixture of 10 g. of α-secondarybutyl hydroxyurethane, 9.6 g. of ethyl iodide and the calculated amount of sodium ethylate in absolute alcohol was treated as described under α-ethyl β-secondarybutyl hydroxyurethane. 6.8 g. of a colorless oil, very slightly soluble in water and boiling at 86.5–87° under 30 mm. pressure were obtained.

Calculated for $C_9H_{19}O_3N$ N, 7 41, found 7 72

(c) *α-Secondarybutyl β Ethyl Hydroxylammonium Chloride,* $\begin{array}{c} H \\ | \\ H - NOC_4H_9 \\ \diagup \diagdown \\ Cl \quad C_2H_5 \end{array}$.
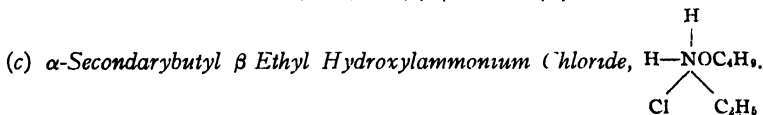
—Five grams of α-secondarybutyl β-ethyl hydroxyurethane were sealed in a tube with a water solution containing 20 g. (large excess) of potassium hydroxide. The tube was heated for 40 hrs. at 98–103°. The contents of the tube were treated as described under α-ethyl β-secondarybutyl hydroxylammonium chloride. 1.8 g. of an oily white solid, too deliquescent to make a melting point determination, were obtained. The chloroplatinate was prepared and precipitated by dry ether as a deep yellow, crystalline solid.

Calc for $[C_2H_5NOC_4H_9H_2]PtCl_6$ Pt, 30 30, found N, 30 11

(d) *α-Secondarybutyl β-Ethyl Hydroxylamine,* $\begin{array}{c} H \\ | \\ N - OC_4H_9 \\ | \\ C_2H_5 \end{array}$.—One and
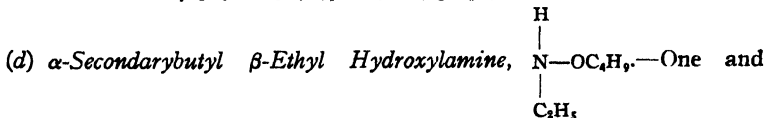
three-tenths grams of the hydrochloride were placed in a distilling flask with 3 g. of powdered potassium hydroxide. Action began at once. The flask was heated gently and a colorless liquid with a distinctly ammoniacal odor was collected in an ice-cooled receiver. Its boiling point was found to be 93.5–94°.

Calc for $C_6H_{15}ON$ N, 11 96, found N, 11 76

IV. The Preparation of α-Secondarybutyl Hydroxylamine.

(a) *α-Secondarybutyl Hydroxylammonium Chloride,* $\begin{array}{c} H \\ | \\ H - N - OC_4H_9 \\ \diagup \diagdown \\ Cl \quad H \end{array}$.—

Ten grams of α-secondarybutyl hydroxyurethane were sealed in a tube with 20 g. of potassium hydroxide dissolved in water and heated at 90–100°, for 28 hrs. The contents of the tube were treated as described above and 2.4 g. of a white, crystalline solid, melting at 54.7–55° and not in the least deliquescent, were obtained. The chloroplatinate was precipitated as beautiful, well defined, deep yellow crystals.

Calc for [C₄H₉ONH₃]₂PtCl₆ Pt, 33 19, found Pt, 32 89

(*b*) α-*Secondarybutyl Hydroxylamine,* H\N—OC₄H₉ —One and eight- H/

tenths grams of the chloride and 5 g. of potassium hydroxide were gently heated in a distilling flask. A clear, colorless liquid with a strongly ammoniacal odor, boiling at 85.5°, was obtained

Calc for C₄H₁₁ON N, 15 72, found N, 15 78

The preparation of α-ethyl β-secondarybutyl and α-secondarybutyl β-ethyl hydroxylamines completes a set of three isomers of the type R₁R₂HNO.

The following table summarizes the properties of the compounds described

	Esters of hydroxyurethane B p	Alkyl hydroxylamines B p	Alkyl hydroxyl ammonium chloride M p
β-Ethyl β-sec -butyl		155–158° (Bewad)	56–57° (Bewad)
α-Ethyl β-sec -butyl	105–106 4° [55 mm]	88 4–89°	94°
α-Sec -butyl β-ethyl	86 5–87 [30 mm]	93 5–94°	[deliquescent]
α-Sec -butyl	116–116 6° [27 mm]	85 5°	54 7–55°

Summary.

(1) The preparation and properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxyurethanes are described in this paper. These compounds are high boiling, oily liquids with a characteristic odor. They reduce neither ammoniacal silver nitrate nor Fehling's solution. They are readily hydrolyzed by potassium hydroxide solution below 100°.

(2) The preparation and the properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxylamines, their chlorides and chloro-platinates are described. The free hydroxylamines are liquids which have a characteristic ammoniacal odor, all boil between 85 and 90° at ordinary pressure, and are reducing agents toward ammoniacal silver nitrate in the cold, and toward Fehling's solution when heated.

CINCINNATI, OHIO

SOME NEW HYDROXYURETHANES AND CHROMOISOMERIC SILVER SALTS OF THEIR ACYL DERIVATIVES.
BY LAUDER WILLIAM JONES AND RALPH OESPER.
Received July 31, 1914

In a recent article[1] we described some experiments which had in view

[1] THIS JOURNAL, **36**, 726 (1914)

the preparation of mixed oximidocarbonic esters, *i. e.*, compounds of the type

$$\begin{array}{c} RO—C—OR^1 \\ \| \\ N—OH \end{array}$$

. It seemed possible to obtain these compounds by

several different methods, but, so far, none of them has proved satisfactory. We have found that the reactions expected either did not occur, or that unstable products were formed which we were not able to isolate, or that isomers of the desired materials were produced. Although we have not been able to work out a general method of preparing mixed oximido-carbonic esters,[1] we have obtained some very interesting results, and an account of these, together with a description of our experiences with the various reactions, form the subject matter of this paper.

Our first experiments were directed toward the preparation of the imido-carbonic esters, since these compounds can be converted into the corresponding oximido esters[1] by treatment with hydroxylammonium chloride. By the action of sodium ethylate on cyanimidocarbonic ethyl ester Nef[2] obtained imidocarbonic ethyl ester:

$$\begin{array}{c} C_2H_5O—C—CN \\ \| \\ NH \end{array} + NaOC_2H_5 = NaNC + \begin{array}{c} C_2H_5O—C—OC_2H_5 \\ \| \\ NH \end{array}$$
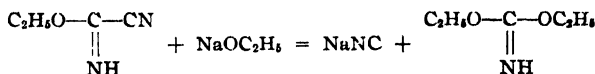
By using other alcoholates in place of sodium ethylate, the mixed imido-carbonic esters might be obtained, from which the oximido esters could be formed:

$$\begin{array}{c} C_2H_5O—C—CN \\ \| \\ NH \end{array} + NaOR = NaNC + \begin{array}{c} C_2H_5O—C—OR \\ \| \\ NH \end{array}$$

$$\begin{array}{c} C_2H_5O—C—OR \\ \| \\ NH \end{array} + NH_2OHCl = \begin{array}{c} C_2H_5O—C—OR \\ \| \\ NOH \end{array} + NH_4Cl$$
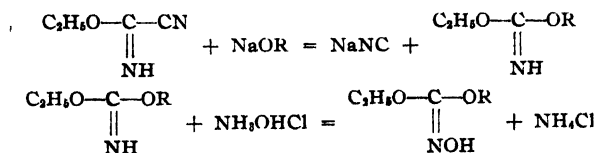
Preliminary experiments indicate that these reactions take place readily when aliphatic alcoholates (including sodium benzylate) are allowed to react with the cyanimidocarbonic ester, but sodium phenolate, and α- and β-naphtholate reacted very slowly, if at all, and then gave rise to thick black oils from which it was not possible to extract any of the desired imidocarbonic esters. A further study of the influence of the acid character of the aromatic alcohols will be made later.

Experiments were also carried out in which attempts were made to extend a method used by Nef[3] for the preparation of cyanimidocarbonic ethyl ester to the other compounds of the type

$$\begin{array}{c} RO—C—CN \\ \| \\ NH \end{array}$$

. By the

[1] Houben and Schmidt, *Ber.*, **46**, 2458 (1913); Jones and Oesper, This Journal, **36**, 729 (1914).

[2] Nef. *Ann.*, **287**, 286 (1895); *Ber*, **46**, 2458 (1913).

[3] Nef, *loc. cit.*, p. 293.

action of potassium cyanide upon an alcoholic solution of bromocyanogen, he obtained cyanimidocarbonic ethyl ester, but when isoamyl alcohol or phenol was substituted for the ethyl alcohol, in the hope of obtaining the corresponding isoamyl or phenyl ester, the chief product of the reaction was a black tar, and the alcohol or the phenol apparently had taken no part in the reaction. When an aqueous solution of the cyanide was slowly added to an ether solution of the bromocyanogen and the alcohol at temperatures not exceeding $-5°$, a greenish yellow oil was formed which changed to a black semi-solid mass as soon as the temperature rose to $10°$. Although these experiments were repeated under the most varied conditions, using dilute or concentrated solutions of the cyanide, or even adding powdered cyanide to a moist ether solution of the other materials, a definite product was not obtained, and further efforts to prepare these compounds in this way were abandoned.

It seemed probable that the mixed oximidocarbonic esters might be prepared by the following method: The salts of the acyl derivatives of carbalkoxyhydroximic acids, when treated with alkyl halides, might be expected to give acylated oximidocarbonic esters.

$$\begin{array}{ccc} \text{MO--C--OR} & & \text{R}^1\text{O--C--OR} \\ \| & + \text{R}^1\text{I} = & \| & + \text{MI} \\ \text{NOC--C}_6\text{H}_5 & & \text{NOC--C}_6\text{H}_5 \\ \| & & \| \\ \text{O} & & \text{O} \end{array}$$
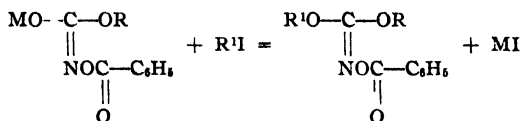
On careful hydrolysis with alkalies, the acyl radical might be eliminated.

$$\begin{array}{ccc} \text{R}^1\text{O--C--OR} & & \text{R}^1\text{O--C--OR} \\ \| & + \text{KOH} = & \| & + \text{C}_6\text{H}_5 \cdot \text{COOK} \\ \text{NOC--C}_6\text{H}_5 & & \text{NOH} \\ \| & & \\ \text{O} & & \end{array}$$
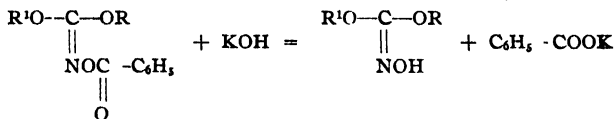
However, the acylated derivatives of the carbalkyloxyhydroxamic acids may exist in two possible forms:

$$\begin{array}{cc} \text{HO--C--OR} & \text{O=C--OR} \\ \| & | \\ \text{NOC--C}_6\text{H}_5 & \text{H--NOC--C}_6\text{H}_5 \\ \| & \| \\ \text{O} & \text{O} \\ \text{(I)} & \text{(II)} \end{array}$$
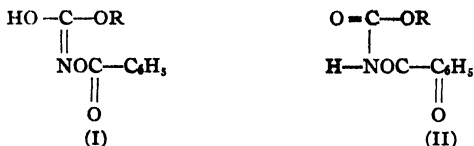
If the *silver salts* correspond to Formula I, then the reaction outlined above might lead to the desired compounds, but if they react according to type (II), isomeric derivatives, $\begin{array}{c} \text{O=C--OR} \\ \| \\ \text{R}^1\text{--NOH} \end{array}$, would be obtained. When such possibilities exist, the silver salt usually gives compounds in which the alkyl group is bound chiefly to oxygen, while the sodium salt leads to the corresponding nitrogen derivative. In the cases investigated so far,

viz., those in which either the ethyl group or the isoamyl group was introduced, we have found that the silver salts gave rise to *nitrogen esters*, since the resulting compounds, when hydrolyzed with hydrochloric acid, yielded β-substituted hydroxylamines, $R-N{\overset{\displaystyle OH}{\underset{\displaystyle H}{\diagdown}}}$. This proved that the alkyl group was bound to nitrogen. Under the same treatment, the isomeric oxygen derivatives would have yielded hydroxylamine itself.

Furthermore, compounds of the form $\begin{array}{c} RO-C-OR \\ \| \\ NO-C-R \\ \| \\ O \end{array}$ have been prepared,

and were found to be crystalline solids, while the nitrogen alkyl derivatives obtained by us were oils, which did not solidify, even when cooled to $-20°$. It is possible that moist silver oxide may form silver salts with the metal bound to oxygen, just as Tafel and Enoch[1] have assumed to be the case for amides, or that some of the other compounds of the type $\begin{array}{c} HO-C-OR \\ \| \\ NOC-R, \\ \| \\ O \end{array}$

may give the desired mixed oximido esters. Then again it may be that the oxygen esters actually were formed first, and that the conditions of our experiments have not been chosen properly to prevent their rearrangement to N-esters, in much the same way that imido esters have been found to rearrange to give alkyl amides.[2]

As a matter of fact, we have found that some of these silver salts may be obtained in two forms, white and yellow, which, under proper conditions, may be converted into one another. It is possible that these may be the *oxygen* and *nitrogen* silver salts, *i. e.*, they may correspond to Formula I and II, respectively. In this case, by choosing the proper conditions, it should be possible to form the desired mixed oximidocarbonic esters. These silver salts will be described at length somewhat later.

Carbethoxyhydroxamic acid (hydroxyurethane), $\begin{array}{c} O-C-OC_2H_5 \\ | \\ H-N-OH \end{array}$, was

first prepared by Hantzsch.[3] Jones[4] modified the method of preparation, and also studied some of its alkyl and acyl derivatives. This modified method has now been applied in the preparation of several of the homologs

[1] Tafel and Enoch, *Ber*, **23**, 104 (1890); Meyer and Jacobson, *Lehrbuch*, Vol. 1, p. 615

[2] Comstock and Wheeler, *Am. Chem. J*, **13**, 522 (1891); Wheeler, *Ibid.*, **21**, 1865 (1899); **23**, 140 (1901).

[3] Hantzsch, *Ber.*, **27**, 1254 (1894).

[4] Jones, *Am. Chem. J.*, **20**, 39 (1898).

of carbethoxyhydroxamic acid, and also the benzyl derivative, H(HO)-N—CO.OC$_7$H$_7$, the first solid compound of this type.

The benzoyl esters of these compounds were readily obtained by treating the aqueous solution of the hydroxamic acid with benzoyl chloride in the presence of potassium carbonate. The silver salts of these esters were precipitated when an aqueous solution of silver nitrate was added to an alcoholic solution of the benzoyl ester, to which an equivalent quantity of ammonium hydroxide had been added.

When treated in this way, all of the compounds investigated produce bright yellow silver salts; but while the yellow color of the methyl, ethyl and propyl compounds was permanent, the yellow precipitates produced in the case of the higher members of the series (*viz.*, isobutyl, isoamyl, benzyl) immediately became colorless. The precipitates separated as curds, and if one of the lumps was broken, the interior was found to be of the original yellow color. Whether the change was due to contact with the alcohol or the water, or whether the phenomenon was a photochemical one has not yet been definitely determined. The *white* salts are much more sensitive to the light than the yellow ones, and blacken readily, even if preserved in an amber desiccator.

Interestingly enough, these salts, both the *yellow and the white*, were slightly soluble in ether, and readily dissolved by chloroform or benzene. When alcohol was added to these solutions, *bright yellow needles* were precipitated, regardless of the original color of the salt. The yellow salts thus produced were perfectly stable, scarcely affected by light, and showed no tendency to change to the white forms at room temperature (see, however, the silver salt of the isoamyl derivative). At higher temperatures, however, the conversion was rapid, and the resulting *white* modifications were also stable; that is, at room temperature, even in contact with the yellow variety they did not revert to the yellow modifications. No decomposition occurred during this change; there was no apparent change in the crystalline form, and both modifications had the same ultimate composition, which was that of the simple silver salts, without any solvent of crystallization. Therefore, the two forms must represent either polymers or tautomers.

In the dry state, the yellow silver salt of the benzoyl ester of carbisoamyloxyhydroxamic acid changed to the white modification rapidly at about 75°, and it seemed possible that the molecular weight in boiling benzene (b. p. 80.5°) might differ from the value determined by the freezing point method in the same solvent. If the same values were obtained, it would argue for a tautomeric change, while if the values were multiples of each other, polymerization would be indicated. The values actually obtained, however, were not conclusive. By both methods of determining the molecular weight, association of two or more molecules was indicated;

and furthermore, the molecular weight of these complexes increased as the concentration of the solutions increased. No change in color was apparent when the solution was raised to the boiling point, and the change which occurs when the dry salt was heated probably does not take place in solution, or proceeds in such a way that equilibrium is reached between the yellow and the white modifications.

All of the *white* salts investigated so far dissolved in chloroform or in benzene to form *yellow* solutions from which alcohol precipitated the *yellow* salts. As mentioned above, when prepared in alcoholic solution, the yellow salts of the compounds with the larger alkyl radicals, became white on the surface where they are in contact with the solvent. Furthermore, if the yellow salts precipitated from chloroform or benzene solutions were dried and then suspended in alcohol, they gradually lost their yellow color and passed over into the *white* form. Therefore, it appears that low temperature and the presence of chloroform, benzene (and ether) favor the yellow form, while alcohol, water and higher temperatures stabilize the white salts. No solvent has been found in which the white salts do not change to the yellow form, so it does not seem possible to determine their molecular weight at present.

All the chemical evidence indicates that the yellow salts have the silver bound to nitrogen, but as these reactions were carried out in the presence of ether, which favors the yellow form, it may be that, if alcohol (which favors the white form) is used as the medium, alkyl halides may react to give compounds in which the alkyl group will be bound to oxygen. Such results, of course, would indicate that the white and yellow salts are tautomeric. These experiments will be carried out. Likewise, attempts will be made to prepare the carbalkyloxyhydroxamic acids containing large aromatic radicals in order to study the effect of such groups on the relative stability of the white and yellow forms.

Experimental Part.

Derivatives of Carbalkyloxyhydroxamic Acids, $\begin{array}{c} O = C-OR \\ | \\ H--N-OH \end{array}$.—The only one of these compounds which has been described is the ethyl derivative prepared by Hantzsch and later by Jones.[1] It seemed desirable to prepare some of the homologs of this compound as they are the materials from which it seemed possible, as outlined above, to obtain the oximidocarbonic esters. The method used by Jones[1] for preparing carbethoxyhydroxamic acid was used to prepare the corresponding methyl, propyl, isobutyl, isoamyl and benzyl derivatives. The procedure was as follows: One equivalent of hydroxylammonium chloride was pulverized and thoroughly mixed with two equivalents of powdered potassium carbonate.

[1] Jones, *Loc. cit.*

The mixture was covered with moist ether and one equivalent of the chloro-carbonic ester was added in small portions, while the flask was cooled by running water. After all the chlorocarbonate was added, the flask was connected with a reflux condenser, and the reaction mixture allowed to stand until the evolution of carbon dioxide had ceased (10 to 12 hours).

$$\begin{array}{c} O{=}C{-}OR \\ | \\ Cl \end{array} + NH_2(OH)Cl + K_2CO_3 = \begin{array}{c} O{=}C{-}OR \\ | \\ H{-}N{-}OH \end{array} + 2KCl + CO_2 + H_2O$$
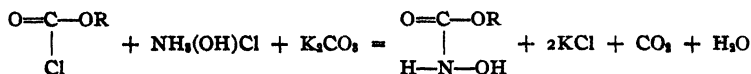
After removing the potassium chloride by filtration, the ether was washed with a small quantity of water, and dried over fused sodium sulfate. The ether was then removed by distillation, and the remaining oil was placed in a desiccator which was exhausted for several hours to remove the last traces of ether. · In this way, colorless or slightly yellow oils possessing characteristic odors were obtained. The benzyl derivative was a crystalline solid. When treated with ferric chloride, solutions of these compounds give a deep blue or purple color reaction. They immediately reduced ammoniacal silver nitrate.

As mentioned above, the benzoyl esters of these compounds,

$$\begin{array}{c} O{=}C{-}OR \\ | \\ H{-}N{-}OC{-}C_6H_5, \\ || \\ O \end{array}$$
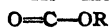
were formed when their aqueous solutions were treated with benzoyl chloride in the presence of potassium carbonate. These esters may be purified by extracting their ether solutions with sodium hydroxide. If carbon dioxide was passed through the alkaline solution, the benzoyl esters were precipitated. However, these compounds were very easily hydrolyzed by dilute alkalies, even in the cold, and some of the product was invariably lost in this way.

I. Derivatives of Carbmethoxyhydroxamic Acid.

Carbmethoxyhydroxamic Acid, $\begin{array}{c} O{=}C{-}OCH_3 \\ | \\ H{-}N{-}OH \end{array}$.—Twenty-five grams of chlorocarbonic methyl ester, 18.4 g. of hydroxylammonium chloride, and 36.5 g. of potassium carbonate produced 21 g. of thick yellow oil which was very soluble in water. This was not analyzed but was converted into its benzoyl ester.

The Benzoyl Ester of Carbmethoxydroxamic Acid, $\begin{array}{c} O{=}C{-}OCH_3 \\ | \\ H{-}N{-}OC{-}C_6H_5.{-} \\ || \\ O \end{array}$

To 9 g. of carbmethoxyhydroxamic acid and 6.8 g. of potassium carbonate dissolved in water, 13.8 g. of benzoyl chloride were added in small portions. A colorless oil separated which soon solidified. After recrystallization

from warm chloroform and ligroin, it formed white needles melting at 82°. The yield was 12.5 g.

> 0 2550 g gave 17 cc N_2 at 29° and 746 mm
> Calc for $C_9H_9O_4N$ N, 7 18   Found N, 7 16%

The compound was soluble in ether, in chloroform and in alcohol, but insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbmethoxyhydroxamic Acid,

$$O = C—OCH_3$$
$$|$$
Ag—N—OC—C_5H_5 —Nine grams of the benzoyl ester described above
$$||$$
$$O$$

were dissolved in alcohol and the equivalent quantity of ammonium hydroxide was added to it. When this solution was treated with 7.8 g. of silver nitrate dissolved in water, a bright yellow precipitate was formed which was separated by filtration, washed with alcohol and water, and dried on a porous plate. Yield, 11 g.

> 0 4870 g gave 0 1735 g Ag
> Calc for $C_9H_8O_4NAg$ Ag, 35 74   Found Ag, 35 62%

The salt melted at 149 150°, was very stable toward light, and was the only one of the silver salts investigated which was not soluble in chloroform or in benzene

II. Derivatives of Carbethoxyhydroxamic Acid.

The Silver Salt of the Benzoyl Ester of Carbethoxydroxamic Acid,

$$O = C —OC_2H_5$$
$$|$$
Ag—NOC—C_6H_5.—Forty grams of this salt[1] were obtained by the action
$$||$$
$$O$$

of 30 g. of silver nitrate on 37 g. of the benzoyl ester of carbethoxyhydroxamic acid. After the salt was dried, it was dissolved in warm chloroform, the solution filtered and cooled to —5°. Alcohol was then added and a mass of bright yellow needles was precipitated. These were collected on a filter, and dried on a porous plate.

> 0 3540 g gave 0 1210 g Ag
> Calc for $C_{10}H_{10}O_4NAg$ Ag, 34 15   Found Ag, 34 18%

The salt was readily soluble in chloroform and in benzene, but only slightly soluble in ether and insoluble in alcohol. When heated to 156–157°, the yellow color faded and a pure white salt resulted which darkens rapidly if the temperature was raised beyond this point. The salt melted with decomposition at 174°. The white form was stable at room temperature though it was much more sensitive to light than the yellow variety was. On ignition, a sample gave the following values.

[1] Jones, *Loc cit*, p 49

0.4356 g. gave 0.1489 g. Ag.

Calc. for $C_{16}H_{13}O_4NAg$: Ag, 34.15. Found: Ag, 34.18%.

The behavior of the yellow silver salt when treated with ethyl iodide or with isoamyl iodide was described in the previous paper,[1] and it will suffice to point out here that the products obtained had the alkyl bound to nitrogen. Samples of these materials which had *not been distilled* gave the same products when hydrolyzed showing that no rearrangement had taken place during the distillation.

Structure of the Yellow Silver Salt.—Provided direct replacement of the metal occurred, the formation of these products indicates that the silver salt has the silver bound to nitrogen. If this be true, it is evident that the compound produced by the action of chlorocarbonic ester on the silver salt of dibenzhydroxamic acid should be identical with the substance formed by the action of benzoyl chloride on the silver salt under discussion. These reactions are shown by the following equations:

$$
\begin{array}{c}
O = C\!-\!OC_2H_5 \\
| \\
Ag\!-\!N\!-\!OC\!-\!C_6H_5 + C_6H_5C\!-\!Cl \\
\qquad\; \overset{||}{O} \qquad\qquad \overset{||}{O} \\
\end{array}
$$

$$
C_6H_5C\!-\!N\!-\!OCC_6H_5 + O = C\!-\!OC_2H_5
$$

$$
\begin{array}{c}
O = C\!-\!OC_2H_5 \\
| \\
C_6H_5C\!-\!N\!-\!OC\!-\!C_6H_5 + AgCl. \\
\overset{||}{O}\quad\;\overset{||}{O}
\end{array}
$$
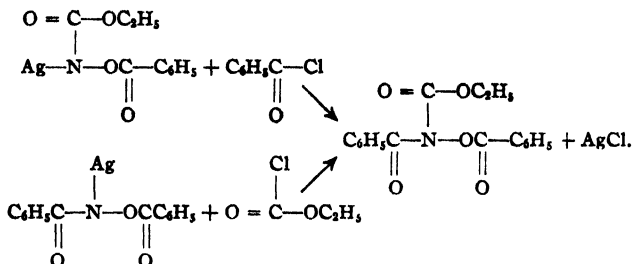
(a) *Action of Benzoyl Chloride on the Silver Salt of Carbethoxyhydroxamic Acid.*—Eleven and five-tenths grams of the silver salt, suspended in ether, were treated with 5 g. of benzoyl chloride. After standing four hours, the silver chloride was separated by filtration, and the ether was removed by distillation. Eight grams of a colorless oil remained, which slowly deposited prismatic crystals. When recrystallized from ether and ligroin, the compound melted at 71–72°.

(b) *Action of Chlorocarbonic Ethyl Ester on the Silver Salt of Dibenzhydroxamic Acid.*—Five grams of the silver salt of dibenzhydroxamic acid[2] were treated with 1.5 g. of chlorocarbonic ethyl ester in the presence of ether. After two weeks, the silver chloride and the unchanged silver salt were removed by filtration, and the liquid evaporated *in vacuo*. After standing for several days, the odor of the ester had disappeared, and the remaining oil slowly solidified. The crystals melted at 71–72°, and a mixture of the products of the reactions described under (a) and (b) melted at the same temperature.

[1] Jones and Oesper, THIS JOURNAL, 36, 729 (1914).

[2] Lossen, *Ann.*, 161, 360 (1872).

The same product, therefore, resulted in both of these reactions, and it was identical with the dibenzoyl ester of carbethoxyhydroxamic acid described by Jones,[1] who prepared it from the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid and benzoyl chloride.

III. Derivatives of Carbpropyloxyhydroxamic Acid.

Carbpropyloxyhydroxamic Acid,
$$O = C—OC_3H_7$$
$$|$$
$$H—N—OH$$
—Twenty-five grams of chlorocarbonic propyl ester were added to a mixture of 14.2 g. of hydroxylammonium chloride and 28 g. of potassium carbonate. 22.5 g. of a thick colorless oil were obtained which were converted into the benzoyl ester.

Benzoyl Ester of Carbpropyloxyhydroxamic Acid,
$$O = C—OC_3H_7$$
$$|$$
$$H—N—OC—C_6H_5.$$
$$\|$$
$$O$$
—

Twenty-seven grams of a colorless oil were obtained by the action of 20 g. of carbpropyloxyhydroxamic acid, 11.5 g. of potassium carbonate and 23.5 g. of benzoyl chloride. All attempts to solidify the oil were unsuccessful. Accordingly, it was dissolved in alcohol, neutralized with ammonium hydroxide and 21 g. of silver nitrate were added to the solution. A bright yellow precipitate was obtained. This was crystallized from chloroform and alcohol, and formed yellow needles which melted at 144–145°.

0.4360 g. gave 0.1418 g. Ag.
Calc. for $C_{11}H_{12}O_4NAg$: Ag, 32.67. Found Ag, 32.32%.

When heated, this salt showed no indication of changing to a white modification.

Dibenzoyl Ester of Carbisopropyloxyhydroxamic Acid,
$$O=C—OC_3H_7$$
$$|$$
$$C_6H_5C—N—OC—C_6H_5.$$
$$\|\quad\quad\|$$
$$O\quad\quad O$$
—Ten grams of the silver salt described above were suspended in ether and 4.2 g. of benzoyl chloride were added. The reaction was completed in three days. The silver chloride was removed by filtration and the ether evaporated in vacuo. Nine grams of a thick oil remained which slowly deposited transparent cubical crystals. These crystals, when recrystallized from chloroform and ligroin, melted at 78–89°.

0.2822 g. gave 11.4 cc. N_2 at 28° and 745 mm.
Calc. for $C_{18}H_{17}O_5N$: N, 4.28. Found: N, 4.36%.

This compound was soluble in ether, in chloroform and in alcohol, but it was insoluble in cold ligroin and in water.

[1] Jones, Loc. cit., p. 50.

The N-Ethyl Derivative of the Benzoyl Ester of Carbpropyloxyhydroxamic

$$O = C - OC_3H_7$$

Acid, $C_2H_5 - N - OCC_6H_5.$ — Fifteen grams of the silver salt described

$$\overset{||}{O}$$

above were suspended in ether, and 7 g. of ethyl iodide were added. After standing two weeks in the dark, the silver iodide was removed, and the other evaporated *in vacuo*. Nine grams of a light yellow oil with a spicy odor remained.

<div align="center">

0.2402 g. gave 12 2 cc N_2 at 22 5° and 735 mm.

Calc. for $C_{18}H_{17}O_4N$: N, 5 53. Found: N, 5 57%.

</div>

When heated in a sealed tube with hydrochloric acid, β-ethyl hydroxyl-ammonium chloride was obtained. This was identified by condensing it with *p*-nitrobenzaldehyde.[1] The product obtained showed that the alkyl group was bound to nitrogen.

IV. Derivatives of Carbisobutyloxyhydroxamic Acid.

$$O = C - OC_4H_9$$

Carbisobutyloxyhydroxamic Acid, $\quad |$. – Twenty-five grams of

$$H - N - OH$$

chlorocarbonicisobutyl ester, 12.8 g. of hydroxylammonium chloride and 25 g. of potassium carbonate produced 21 g. of a colorless oil which was not very soluble in water. When treated with copper acetate solution it produced a crystalline green precipitate which was not affected when boiled with water.

$$O = C - OC_4H_9$$

Benzoyl Ester of Carbisobutylhydroxamic Acid, $\quad H - N - OC - C_6H_5.$ —

$$\overset{||}{O}$$

A colorless oil was produced by the action of 19 g. of benzoyl chloride, 9.4 g. of potassium carbonate and 18 g. of carbisobutyloxyhydroxamic acid. This was dissolved in ether and extracted with dilute sodium hydroxide. The alkaline solution was cooled to 5° and carbon dioxide was passed with the solution. A crystalline precipitate appeared. When recrystallized from warm chloroform and ligroin it formed needles melting at 43–44°. Yield, 19 g.

<div align="center">

0 2944 g. gave 16 5 cc. N_2 at 28° and 751 mm.

Calc. for $C_{12}H_{15}O_4N$. N, 5.90   Found: N, 6.09%.

</div>

The compound was soluble in ether, in chloroform and in alcohol, but was insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbisobutyloxyhydroxamic Acid,

[1] Hantzsch and Hillard, *Ber.*, **31**, 2066 (1898).

O=C—OC$_4$H$_9$
|
Ag—N—OC—C$_6$H$_5$.—An alcoholic solution of 21.5 g. of the benzoyl
‖
O
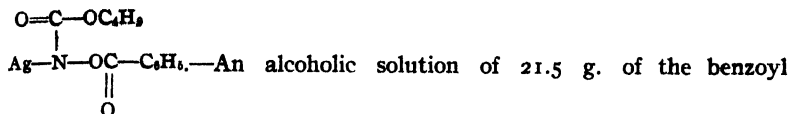
derivative was treated with one equivalent of ammonium hydroxide, and then with an aqueous solution of 15 g. of silver nitrate. A bright yellow precipitate was formed which immediately became colorless where it was in contact with the solvent. The interior of the precipitate was still yellow after standing five minutes. The precipitate was collected on a filter, thoroughly washed with alcohol, and dried on a porous plate placed in an amber desiccator. After standing over night, the entire mass had blackened. This material was extracted with warm chloroform, the solution cooled to —5° and an excess of alcohol added. Bright yellow needles were precipitated.

> 0 2492 g gave 0 0784 g Ag
> Calc for C$_{12}$H$_{14}$O$_4$NAg Ag, 31 37   Found Ag, 31 46%

When warmed to 80–82°, the yellow crystals become white. The white mass softened slightly at 144° and finally melts at 158°. The white form did not change to the yellow form at room temperature. A sample of the white salt, on ignition, gave the following values

> 0 4230 g gave 0 1325 g Ag
> Calc for C$_{12}$H$_{14}$O$_4$NAg Ag, 31 37. Found Ag, 31 32%

The conversion of the yellow form into the white form took place very slowly at 40°, but the change occurred only in certain parts of the mass and the rest of the material remained yellow. Furthermore, the change appeared to commence in the interior of these regions and to spread outward, which would seem to indicate that the phenomenon is not of a photochemical nature. The most curious effect, however, was observed if the portion of the white form was rubbed against a hard surface with a porcelain spatula. Where it was rubbed, a bright yellow streak appears which immediately becomes colorless again. The rapidity of the reversion to the white form seemed to be influenced by the intensity of the light, for the change was almost instantaneous in direct sunlight, slower in diffused light, while if the salt is rubbed in the dark it remains yellow until brought into the light. No explanation of this peculiar behavior is offered.

The N-Ethyl Derivative of the Benzoyl Ester of Carbisobutyloxyhydroxamic
O=C—OC$_4$H$_9$
|
Acid, C$_2$H$_5$—N—OC—C$_6$H$_5$.—Twenty-one and five-tenths grams of the
‖
O
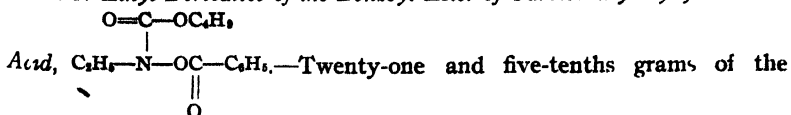
yellow silver salt described above were suspended in ether, and 10 g. of ethyl iodide added. The reaction was complete after two weeks. A

bright yellow oil with a spicy odor was obtained when the ether was evaporated. Yield, 14 g.

<div style="text-align:center">

0 3096 g gave 15 6 cc at 29° and 740 mm
Calc for $C_{14}H_{16}O_4N$ N, 5 28   Found N, 5 37%

</div>

When heated in a sealed tube with concentrated hydrochloric acid for six hours at 110°, β-ethyl hydroxylammonium chloride was obtained, showing that this was the nitrogen derivative.

<div style="text-align:center">

V. Derivatives of Carbisoamyloxyhydroxamic Acid.

</div>

Carbisoamyloxyhydroxamic Acid,

$$O = C—OC_5H_{11}$$
$$|$$
$$H—N—OH$$

.—Twenty-five grams of chlorocarbonicisoamyl ester, 11.5 g. of hydroxylammonium chloride and 22.8 g. of potassium carbonate were allowed to react in the usual manner, and 23 g. of a thick, light yellow oil were obtained. The compound had a slight odor suggestive of isoamyl alcohol and was only slightly soluble in water. Copper acetate produced a green crystalline precipitate from an alcoholic solution which was not affected when boiled with water.

The Benzoyl Ester of Carbisoamyloxyhydroxamic Acid,

$$O = C—OC_5H_{11}$$
$$|$$
$$H—N—OC—C_6H_5.$$
$$||$$
$$O$$

– All attempts to obtain this compound in the solid state were fruitless. The product of the reaction of carbisoamyloxyhydroxamic acid, potassium carbonate and benzoyl chloride was a colorless oil, which, when dissolved in sodium hydroxide and precipitated by carbon dioxide, remained liquid even when thoroughly dried and cooled to —10° for several hours. It was very easily hydrolyzed by dilute alkalies, and the yield was extremely poor if the compound was purified in this way.

Silver Salt of Carbisoamyloxyhydroxamic Acid.

$$O=C   OC_5H_{11}$$
$$|$$
$$Ag—N—OC—C_5H_5. —$$
$$||$$
$$O$$

The silver salt was precipitated from an alcoholic solution of the benzoyl ester in the form of bright yellow curds which turn white immediately. After drying the salt over night, it was dissolved in warm chloroform and reprecipitated by alcohol in the form of bright yellow needles.

<div style="text-align:center">

0 4506 g gave 0 1354 g Ag
Calc for $C_{13}H_{16}O_4NAg$ Ag, 30 13   Found Ag, 30 06%

</div>

When heated to 40°, the salt turned white in patches, and at about 75°, the change was rapid and complete   If the temperature was raised still higher, no further change occurred until the salt melted at 141-142°. The white form, on ignition, gave the following results.

о 3632 g gave o 1090 g Ag

Calc for $C_{14}H_{16}O_4NAg$ Ag, 30 13   Found Ag, 30 01%

This white form showed no tendency to revert to the yellow modification, even in contact with a particle of the latter at $-10°$. On one occasion, however, the yellow form was precipitated as usual from a chloroform solution by alcohol, and as soon as the crystals were separated from the solvent by filtration they began to turn white. However, the change was localized, and after two weeks the yellow and the white forms still existed side by side. We have never been able to duplicate this change at room temperature.

As was stated above, it seemed possible that molecular weight determinations might throw some light on the nature of this color change. The figures obtained in freezing benzene gave values which varied from 739 to 1514 depending on the concentration of the solution, and the values in boiling benzene, using Menzies[1] method, were of the same order The value for the simple salt is 538

Dibenzoyl Derivatives of Carbisoamyloxyhydroxamic Acid,

$$O=C—OC_5H_{11}$$

$$C_6H_5C—N—OC—C_6H_5. $$
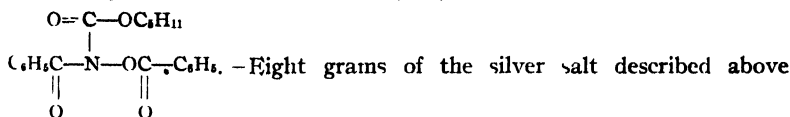
—Eight grams of the silver salt described above
were treated with 3 1 g. of benzoyl chloride. The reaction was completed after 2 weeks and 5 g. of a colorless oil were obtained on evaporating the ether After standing in an exhausted desiccator for 10 days, clear prismatic crystals were deposited, which, after recrystallization from warm ligroin, melted at 69-70°.

о 3050 g gave 11 cc. N_2 at 26° and 749 5 mm

Calc for $C_{20}H_{21}O_5N$ N, 3 94   Found N 3 95%

The compound is soluble in ether, in chloroform and in alcohol, slightly soluble in ligroin and insoluble in water.

The Ethyl Derivative of the Benzoyl Ester of Carbisoamyloxyhydroxamic

$$O = C—OC_5H_{11}$$

Acid, $C_2H_5—N—OCC_6H_5.$—Eleven grams of the yellow salt and 4.8 g.

$$O$$
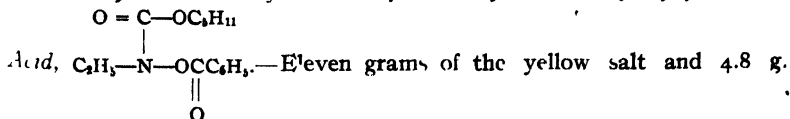
of ethyl iodide were allowed to react in the presence of ether for two weeks. A light yellow oil remained when the ether evaporated.

о 4323 g gave 20 cc N_2 at 25° and 745 mm.

Calc for $C_{15}H_{21}O_4N$ N, 5 01. Found. N, 5 06%

It gave β-ethylhydroxylamine upon hydrolysis.

[1] Menzies, THIS JOURNAL, **32,** 1615 (1910)

VI. *Derivatives of Carbbenzyloxyhydroxamic Acid:*

Carbbenzyloxyhydroxamic   Acid,

$$O = C = OCH_2C_6H_5$$
$$|$$
$$H-N-OH$$

.—Forty grams of chlorocarbonic benzyl ester, 16.2 g. of hydroxylammonium chloride and 32.4 g. of potassium carbonate produced a thick yellow oil which solidified on standing over night.   When recrystallized from chloroform and ligroin, the compound was obtained in shining scales melting at 65°.   Yield, 30 g.

o 2530 g gave 19 4 cc N₂ at 28° and 747 5 mm
Calc for C₈H₉O₃N N, 8 38   Found N, 8 29%

The compound was insoluble in ether, in alcohol and in chloroform, somewhat soluble in water and insoluble in cold ligroin.

The Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,

$$O=C-OCH_2C_6H_5$$
$$|$$
$$H-N-OC-C_6H_5$$
$$\|$$
$$O$$

.

—Eighteen and five-tenths grams of carbbenzyloxyhydroxamic acid were treated with 7.46 g. of potassium carbonate and 15.6 g. of benzoyl chloride. An oil separated which was soon solidified.   When recrystallized from warm alcohol and ligroin it formed white needles melting at 109–110°.

o 2944 g gave 13 6 cc N₂ at 23 5° and 748 5 mm
Calc for C₁₅H₁₃O₄N N, 5 16   Found N, 5 12%

The compound was soluble in alcohol, in ether and in chloroform, and insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,

$$O = C-OCH_2C_6H_5$$
$$|$$
$$Ag-N-OC-C_6H_5$$
$$\|$$
$$O$$

.—Sixteen grams of the benzoyl ester, when treated with ammonium hydroxide and 10.3 g. of silver nitrate gave a yellow precipitate which immediately turned white.   When recrystallized from chloroform and alcohol it formed bright yellow needles which melted at 150–151°.

o 3583 g gave o 1025 g Ag.
Calc for C₁₅H₁₂O₄NAg Ag, 28 67.   Found Ag, 28 61%.

.The salt became white when heated, but the transition temperature was so near the melting point that it was not possible to isolate the white form in this way.

Ethyl Derivative of the Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,

$$O=C-OCH_2C_6H_5$$
$$|$$
$$C_2H_5-N-OC-C_6H_5$$
$$\|$$
$$O$$

.—Eight grams of the silver salt described above

were allowed to react with 2.3 g. of ethyl iodide for one week.   5 g. of a light yellow oil were obtained.

> 0.4658 g. gave 20 cc N_2 at 21° and 745 mm.
> Calc. for $C_{17}H_{17}O_4N \cdot N$, 4 68   Found N, 4 81%

Summary.

1. In the course of experiments which had in view the preparation of mixed oximidocarbonic esters, $RO.C(NOH).OR'$ several new hydroxy-urethanes, including the methyl, isopropyl, isobutyl, isoamyl and benzyl derivatives were prepared, and their benzoyl esters studied.

2. The silver salts of some of these benzoyl esters were obtained in two modifications, white and yellow, of the same composition and mutually transformable.   While the methyl, ethyl and isopropyl derivatives were prepared only as yellow salts, the compounds with larger radicals, *viz.*, isobutyl, isoamyl, and benzyl, were obtained in two forms.

3. These silver salts have been found to yield derivatives with the alkyl groups bound to *nitrogen* instead of to *oxygen*.   This unforseen re-action prevented us from obtaining the acyl derivatives of mixed oximido-carbonic esters, which would otherwise have resulted from the action of various alkyl halides upon these silver salts.

CINCINNATI, OHIO.

THE ISOLATION OF CRYSTALLINE *dl*-GLYCERIC ALDEHYDE FROM A SYRUP OBTAINED BY THE OXIDATION OF GLYCEROL.

BY EDGAR J. WITZEMANN.

dl-Glyceric aldehyde is a compound of considerable importance.   In the various more or less theoretical discussions of the break-down and synthesis of the hexoses, either in the chemical laboratory or in the living organism, *dl*-glyceric aldehyde, along with dihydroxyacetone, assumes a prominent place.   The collection of facts with regard to its behavior in the body has been retarded by the difficulty of obtaining sufficient quantities with which to work.   The only method now known of preparing the pure substance is that of Wohl, and this method is extremely laborious. For physiological experiments in man, quantities are required which make Wohl's method well nigh prohibitive.   The method of Fenton and Jackson is simple and undoubtedly gives a large yield of glyceric aldehyde, although admixed with impurities.   Dr. R. T. Woodyatt, of this laboratory, some-time ago published a preliminary report on the use of glyceric aldehyde, prepared according to the latter method, in diabetes mellitus.[1]   The nature of these results was such as to emphasize the necessity of determining

[1] *J. Am. Med. Assoc.*, **55**, 2109–2112 (1910).

more definitely than has yet been done the composition of the crude glyceric aldehyde syrup employed and if possible to develop a method for purifying it.

The only known compound of glyceric aldehyde which would serve for its identification, and which could also be subsequently used as a source of free glyceric aldehyde, is glyceric aldehyde diethyl acetal. If, therefore, glyceric aldehyde diethyl acetal could be made from the Fenton and Jackson reaction mixture it would at once prove, more conclusively than has yet been done, the presence of glyceric aldehyde and also serve for its isolation. The following paper is a report on the successful execution of the plan outlined above, as suggested by Dr. Woodyatt.

When glycerol is acted upon by one atom of oxygen two oxidation products are theoretically possible, namely:

$$
\begin{array}{ccc}
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CHO
\end{array}
& \text{and} &
\begin{array}{c}
CH_2OH \\
| \\
CO \\
| \\
CH_2OH
\end{array} \\
\text{Glyceric aldehyde.} & & \text{Dihydroxy acetone.}
\end{array}
$$

The preparation of pure dl-glyceric aldehyde, or any derivative from which pure glyceric aldehyde itself can be isolated, from an oxidation product of glycerol has apparently been frequently tried but without success. In fact, in most cases in which the presence of glyceric aldehyde has been reported its identity was established through the formation of phenyl-glycerosazone with phenylhydrazine, which, however, is produced by both of the oxidation products given above.[1] This reagent will, therefore, not help in deciding which of the above compounds, or whether both, are present in a reaction mixture.

Since the literature on the formation of glyceric aldehyde by oxidation methods is very scattered it may be well to give a brief history of this subject at this point. J. van Deen[2] observed that either an electrical current or nitric acid acting on glycerol gave an optically inactive, fermentable syrup, which reduced cupric oxide in alkaline solution and which he considered to be a sugar. Huppert,[3] Kirchner and Meissner,[4] Heynsius,[5] Perl[6] and G. Werther[7] all disputed v. Deen's results as a whole or in part.[8] Przibytek[9] found that prussic acid acting on glycerol gives some glyceric

[1] Fischer and Tafel, Ber., 20, 1088 (1887).

[2] Nederl. Tydschr. v. Geneesk., 4, Aug., 1860.

[3] Arch. f. Heilkunde, 3, 289 (1862).

[4] Z. ration. Med., [3] 16, 289 (1862).

[5] Nederl. Tydschr. v. Geneesk., 6, 641 (1862).

[6] Konigsberger Med. Jahrb., 8, 84 (1862); J. prakt. Chem., 88, 148 (1862).

[7] J. prakt. Chem., 88, 151 (1862).

[8] For a good account see Chem Zentr., 1863, 833–41; or Jahrb. f. Chem., 1863, 501.

[9] J. Russ. Chem. Soc., 12, 214 (1887); 13, 330 (1888).

aldehyde in addition to meso-tartaric and saccharic(?) acids. Grimaux[1] oxidized glycerol with platinum black and states that he obtained "glyceric aldehyde" which was fermentable. Fischer and Tafel[2] oxidized glycerol with nitric acid and got a compound which reduced Fehling's solution in the cold and gave the phenylglycerosazone. They challenge Grimaux's right to priority on the ground that he identified his so-called glyceric aldehyde only by its ability to reduce alkaline copper solutions. A short time later they synthesized acrose[3] by hydrolyzing acrolein bromide and concluded that glyceric aldehyde must be an intermediate in the synthesis of this compound. Later[4] they prepared a product which they declared was probably glyceric aldehyde, (1) by the oxidation of glycerol with bromine in the presence of soda and (2) by the oxidation of lead glycerate with bromine vapors. They subsequently decided that these products were chiefly dihydroxyacetone[5] without definitely proving that there was any glyceric aldehyde present at all. Later Wohl and Neuberg[6] showed by means of the phloroglucinol test that the product obtained in (1) is mainly, if not solely, dihydroxyacetone, while the product obtained in (2) is also mainly dihydroxyacetone but contains a little glyceric aldehyde, since it gave a slight positive phloroglucinol test. Piloty and Ruff[7] had previously shown that the product in the latter case gave a large amount of dihydroxyacetoxime, from which they likewise concluded that this crude oxidation syrup consisted for the most part of dihydroxyacetone. W. E. Stone and McCoy[8] probably obtained traces of glyceric aldehyde or dihydroxyacetone, as shown by qualitative tests when solutions of glycerol containing sulfuric acid or sodium nitrate were electrolyzed. Likewise Fonzes-Diacon[9] obtained detectable quantities of "glycerose" by the action of mercuric chloride on glycerol. Lobry de Bruyn[10] found that the hydrolysis of dibromoacrolein gave detectable quantities of "glyceric aldehyde." Wohl[11] synthesized glyceric aldehyde from acrolein by preparing acrolein diethyl acetal which, when oxidized with potassium permanganate under the prescribed conditions, gave glyceric-

[1] *Compt. rend.*, **104**, 1276 (1887); *Chem. Zentr.*, **1887**, 629; *Bull. soc. chim.*, **45**, 481 (1886).

[2] *Ber.*, **20**, 1088 (1887); *Chem. Zentr.*, **1887**, 691.

[3] *Ibid.*, **20**, 2566 (1887); **1887**, 1491.

[4] *Ibid.*, **20**, 3384 (1887); **21**, 2634 (1888); **1888**, 277, 1303.

[5] *Ibid.*, **22**, 106 (1889); **1889**, I, 278.

[6] *Ber.*, **33**, 3098, 3109 (1900).

[7] *Ibid.*, **30**, 1663 (1897).

[8] *Am. Chem. J.*, **15**, 656 (1893); *Chem. Zentr.*, **1894**, I, 199.

[9] *Bull. soc. chim.*, [3] **13**, 862 (1895); *Chem. Zentr*, **1895**, II, 676.

[10] *Rec. trav. chim.*, **17**, 258 (1898); *Chem. Zentr.*, **1898**, II, 964.

[11] *Ber.*, **31**, 1796, 2394 (1898); *Chem. Zentr.*, **1898**, II, 419, 1008; see also Wohl and Neuberg, *Ber*, **32**, 1352 (1899); **33**, 3095 (1900); *Chem. Zentr.*, **1899**, I, 1272; **1900**, II, 1197.

aldehyde diethyl acetal. Glycericaldehyde diethyl acetal on hydrolysis in 0.1 N sulfuric acid gave dl-glyceric aldehyde. This was the first time that this compound had been prepared in pure form. The next year (1899) Fenton and Jackson[1] reported on the oxidation of glycerol with hydrogen peroxide in the presence of 10% of ferrous sulfate. The syrup product of this reaction reduced Fehling's solution in the cold, gave the reaction for aldehydes with Schiff's reagent and yielded phenylglycerosazone with phenylhydrazine. They treated a portion with prussic acid according to the method of Fischer and Tafel.[2] Trihydroxyisobutyric acid, which should have been formed if dihydroxyacetone was present, could not be found. When another portion was treated with the calculated quantity of hydroxylamine there was no sign of the formation of dihydroxyacetoxime crystals.[3] Fenton and Jackson, therefore, concluded that the product obtained by them probably consisted chiefly of dl-glyceric aldehyde. Ciamician and Silber[4] observed that glycerol is oxidized to "glycerose" by quinone, which is simultaneously reduced to quinhydrone. By the action of ozone on glycerol Harries[5] obtained glyceric aldehyde or dihydroxyacetone as shown by the formation of phenylglycerosazone with phenylhydrazine. Seyewetz and Gibello[6] found that trioxymethylene and sodium sulfate gave a sugar-like compound in which "formose" and "glycerose" have been found. When glycerol is treated with sodium hypochlorite in the presence of cobalt chloride,[7] or sodium hypochlorite and chlorine in the presence of cobalt chloride "glycerose," identified as the phenylosazone, is formed. Neuberg[8] obtained some dl-glyceric aldehyde by the electrolysis of dl-erythronic acid, and in similar products from d-galactonic acid, d-lyxose, dl-erythronic acid[9] and l-arabonic acid.[10] Neuberg also found[11] that a 5% aqueous solution of glycerol, containing 0.8% of uranium sulfate, when exposed for six hours to June sunlight developed a reducing power equal to 2.1% solutions of glucose, which corresponds to a 42% transformation. Glyceric aldehyde was identified by the formation of the phenylosazone, by a re-

[1] *J Chem Soc*, **75**, 4 (1899), *Chem. News*, **78**, 187 (1898), *Chem Zentr*, **1898**, II, 1011, **1899**, I, 249, 521

[2] *Ber*, **22**, 106 (1889)

[3] Piloty, Ruff, *Ibid*, **30**, 1663 (1897)

[4] *Atti accad Lincei*, [5] **10**, I, 92 (1901), *Chem Zentr*, **1901**, I, 770

[5] *Ber*, **36**, 1933 (1903), *Chem Zentr*, **1903**, II, 189

[6] *Compt rend*, **138**, 150 (1904), *Chem Zentr*, **1904**, I, 581

[7] Tarugi, *Gazz chim ital*, **36**, I, 332 (1906), *Chem Zentr*, **1906**, II, 558

[8] *Biochem Ztschr*, **7**, 527 (1907), *Chem Zentr*, **1908**, I, 1165, *C A*, **2**, 1724

[9] Neuberg, Scott, Lachmann, *Biochem Ztschr*, **24**, 152 (1910), *Chem Zentr*, **1910**, I, 1231, *C A*, **4**, 1474

[10] Neuberg and Hirschberg, *Biochem Ztschr*, **27**, 327 (1910), *Chem Zentr*, **1910**, II, 1455, *C A*, **5**, 313

[11] *Biochem Ztschr.*, **13**, 307 (1908), *Chem Zentr*, **1908**, II, 1485, *C A*, **3**, 2142.

duction of Fehling's solution in the cold, by the absence of the characteristic reaction with resorcinol and by the formation of a glucoside-like crystalline compound with phloroglucinol.[1]

Experimental Part.

The crude glyceric aldehyde syrup was prepared essentially as described by Fenton and Jackson.[2] 100 g. of glycerol in 100 cc. of water, to which 5 or 10 g. of ferrous sulfate—previously dissolved in 15 cc. of water—have been added, are placed in a two liter flask. 771 cc. of 6% hydrogen peroxide (1.25 mols hydrogen peroxide for 1 mol glycerol) were added at the rate of about 100 cc. in an hour, care being taken to avoid a rise in temperature of more than 5° to 7°. After adding a portion of 50 to 100 cc. of the hydrogen peroxide, it seems desirable to wait before adding subsequent portions until the red color of the reaction mixture has faded somewhat. When all of the hydrogen peroxide has been added the mixture is allowed to stand 24 hours in order to allow the oxidation to continue until the solution becomes clear and pale yellow in color.[3]

[1] See also Neuberg, *Z. physiol. Chem.*, **31**, 564 (1900); *Zt. ver. Rub.-Ind.*, **1901**, 270.

[2] *Loc cit.*

[3] The result obtained in the oxidation of glycerol with hydrogen peroxide may vary quite widely. On one occasion the attempt was made to prepare some of this syrup in a shorter time. The same quantities of materials were used as given above; the mixture was kept constantly in an ice-water bath. The only difference in procedure was that the hydrogen peroxide was all added a little at a time in the course of 5 hours. This reaction mixture did not become pale yellow in color on standing for 2 days; it remained quite red. The reaction mixture was strongly acid and showed, by titration with Fehling's solution, some 22% of the sugar theoretically derivable from 100 g. of glycerol. In the meantime Dr. Nef, of the University of Chicago, had become interested in these experiments and was conducting a series of quantitative experiments in order to determine something more about the limits of this reaction. His quantitative data would indicate that the amount of acid formed increases, and the amount of sugar formed decreases as the length of time is diminished during which the hydrogen peroxide is added. Likewise, he found that, if the hydrogen peroxide is added very slowly (drop by drop for example), much acid and little sugar are formed. In order, therefore, to get more definite data on the best mode of procedure in this oxidation, the following experiment was made:

100 grams of glycerol (pure double distilled) and 10 grams of ferrous sulfate (precipitated by alcohol) in 100 cc. of water were treated with 784 cc. of 5.89% hydrogen peroxide (or 1.25 molecules), at the following rate: 45 cc. were added in the first hour, 65 cc. in the 2nd hour, 70 cc. in the 3rd hour, 85 cc. in the 4th hour, 100 cc. in the 5th and 6th each, 110 in the 7th, 120 cc. in the 8th, and the remainder (90 cc.) in 40 minutes more. All of the hydrogen peroxide was added in one working day. The mixture was kept in ice-water throughout the experiment. The temperature of the reaction mixture was, as a rule, 10°, sometimes 8°, rising usually to 12°, but sometimes to 15°, on adding the hydrogen peroxide. The peroxide was added in small portions at first (2–3 cc.) but in the later stages as much as 10 cc. were added at one time. This mixture, on standing in the refrigerator over night, had become pale yellow in color and gave a negative test for hydrogen peroxide. It had a perceptible odor of formaldehyde

This solution is then neutralized at room temperature as completely as possible by simply shaking with an excess of powdered calcium carbonate.[1]

The sediment (chiefly excessive calcium carbonate) is filtered off by means of a suction filter. The filtrate is then concentrated to a syrup by distilling *in vacuo* (bath temperature 40–45°), during which process a considerable quantity of calcium salts separate in the bottom of the flask (mostly calcium sulfate). The residue from the distillation is then mixed with four to five volumes of absolute alcohol containing some ether. This solution is then freed from its precipitate by sedimentation and filtration and again reduced to a thick, clear, pale yellow syrup by distilling *in vacuo* (bath temperature not over 45°). The total yield of syrup is 70 to 80 g. By extracting the sediment of calcium salts, etc., with another portion of alcohol somewhat more material may be recovered.

The final product has a sweet taste accompanied by a slightly aromatic sour or sometimes a bitter taste. This latter taste is probably due in part to the diethyl acetal of glyceric aldehyde. The amount of it seems to increase with the amount of free acid left unneutralized by the calcium carbonate and the time during which the aldehyde remains in the absolute alcohol solution. The syrup, on heating, gives the odor of burnt sugar and leaves a slight residue on ignition. Fehling's solution is reduced slowly in the cold, in a minute or two at room temperature and instantly at 50°. If 10 cc. of a 1% solution are treated with 1 cc. of 20% potassium hydroxide and the alkaline mixture allowed to stand for half an hour, or if it is heated to boiling, its ability to reduce Fehling's solution at room temperature is lost but the solution retains its power to reduce Fehling's solution on boiling. The above change indicates acrose (hexose) formation. The reducing power of the syrup, as determined with Fehling's solution, is frequently 52-58% of that of pure glucose. With Schiff's reagent it gradually gives the characteristic color tests for aldehydes. By treating with phenylhydrazine in the usual way an osazone is readily formed, which, after recrystallization from 50% alcohol and then from benzene, gives a melting point of 130–1° (phenylglycerosazone). When several drops of a 0.25% solution of this sugar-containing syrup were warmed with

and when titrated with Fehling's solution showed a glucose equivalent corresponding to 38% of that which could occur if all the glycerol had been converted into glucose

A parallel experiment in which only 1 o molecule of hydrogen peroxide was added during the same period showed about the same amount of sugar and less formaldehyde and free acids   These solutions were turned over to Dr Nef

It is quite possible that a further variation of conditions might serve to increase the yield in sugar by 5 to 15%   Experiments will be made on this point

[1] If this material is not to be used for physiological experiments it is better to use barium carbonate to neutralize the free acid because barium sulfate is so much less soluble.

0.5 cc. of a cold saturated phloroglucinol solution, in the presence of a trace of sulfuric acid, a flocculent precipitate was formed in about one minute when the mixture was placed in hot water. This precipitate corresponds well with the description of the glucoside-like compound between phloroglucinol and glyceric aldehyde as given by Wohl and Neuberg.[1]

All of the above stated facts harmonize well with the supposition that the syrup contains chiefly *dl*-glyceric aldehyde, as maintained by Fenton and Jackson, but they do not prove it conclusively since a mixture of aldo- and keto-trioses would give similar reactions.

A method of separating the glyceric aldehyde from any dihydroxyacetone or other impurities that may be present in the mixture, was needed. It was thought that the acetal derivative would enable this to be done. Wohl not only synthesized glyceric aldehyde by the hydrolysis of its acetal but also demonstrated that the aldehyde could be converted back into the acetal[2] by the method used by Fischer and Giebe,[3] which consists in dissolving the aldehyde in absolute alcohol containing 1% of dry hydrochloric acid gas, and allowing the mixture to stand five days in the cold, after which it is worked up for the acetal. Ketones react very much more difficultly to form acetals under these conditions.[4] In fact the acetal of dihydroxyacetone is not known as yet. It was hoped, therefore, to convert the glyceric aldehyde of the Fenton and Jackson mixture into the acetal by the method of acetylating used by Fischer and Giebe, to remove and purify the acetal by fractional distillation and finally to liberate pure glyceric aldehyde from the acetal so formed in accordance with the method used by Wohl.

The following is a brief record of the experiments made in the preparation of *dl*-glyceric aldehyde diethyl acetal:

(a) Ten grams of the crude glyceric aldehyde were dissolved in 87 cc. of absolute alcohol and cooled to 0°. 13 cc. of 8.5% dry hydrochloric acid gas in absolute alcohol were added and the mixture placed in a refrigerator at 0°. The reducing power of this solution was tested, from time to time, with Fehling solution and finding no further loss at the end of three weeks, it was worked up as follows: The solution was treated with an excess of lead carbonate in order to remove the hydrochloric acid. On filtering, a clear, reddish yellow solution was obtained, which was concentrated by distilling *in vacuo* at 21–22°. No tar was formed. A hot ceresin bath (150°) was now placed around the flask. Distillation began at a low temperature and the rise in temperature was slow up to 60°, rapid from 60° to 110°, and slow from 110° to 144°, at which point it

[1] *Ber*, **33**, 3095 (1900).
[2] *Ibid*, **33**, 3103.
[3] *Ibid.*, **30**, 3055; **31**, 545
[4] Meyer u Jacobson, "Lehrb. d. Org. Chem," 2nd Ed., Vol I, 1, p. 64.

remained a moment before dropping quickly to 138°. The pressure was 22 to 25 mm. throughout the distillation. The distillate between 110° to 144° showed a strong acid reaction and reduced Fehling's solution in the cold. The drop of colorless liquid on the thermometer did not reduce Fehling's solution in the cold. The unsatisfactory results of this experiment are due largely to the presence of acid, as will appear in the following experiments:

(b) Sixty grams of the crude aldehyde were treated as in (a) and after remaining at 0° for one month the reaction mixture was worked up. The addition of a little water made it possible to completely neutralize the solution with lead carbonate. The alcohol was removed by distilling *in vacuo* as before. The residue was diluted with an equal volume of water and saturated with finely powdered potassium carbonate.[1] The mixture was cooled from time to time as it became perceptibly warm. Toward the end the solution separated in two layers, the upper one of which was a red oil. Sufficient ether was then added to dissolve the upper layer. The solution was extracted four more times with ether. The ether solution was filtered through a dry filter and dried over night with anhydrous sodium sulfate. After driving off the ether this oil distilled at 134° at 15 mm. pressure (ceresin bath at 150°). The thick oily distillate had only a very slight yellowish tinge and an acrid burning taste. Yield, estimated 4 or 5 g.

(c) The experiment was repeated as in (b) except that the residue after distilling off the alcohol was extracted at once with ether and not treated with water and potassium carbonate as in (b). This gave 19.5 g. of a thick, golden yellow oil. When this oil was distilled *in vacuo* two fractions were obtained, one boiling mostly below 80°, the other between 132-40° at 18 mm. The latter weighed 4 g. and subsequently proved to be nearly pure glyceric aldehyde diethyl acetal. A large quantity of a dark red, tarry liquid remained in the flask. Subsequently a higher boiling fraction of unknown composition, boiling mostly at 155-70° at 18 mm., was obtained from this residue. This method is less satisfactory than that used in (b).

(d) Experiment (b) was repeated using 320 g. of crude aldehyde. In the distillation two fractions were collected. The first consisted of 11.5 g. of material distilling below 120° at 11 mm. pressure. The second was 41 g. distilling between 120° and 140° at the same pressure. When the low boiling or first distillate was redistilled 10.1 g. distilled below 110° at 11 mm. When the high boiling or second distillate was placed in the flask containing the small residue of the previous distillation it was found that distillation began at 112° at 11 mm. pressure. The temperature arose rapidly to 119°, then slowly to 121° at which point the larger part

[1] Wohl, *Ber.*, **31**, 1796 (1898); **33**, 3099 (1900).

of the distillate passed over. The temperature then rose fairly rapidly to 123°, and the distillation was interrupted at this point. The temperature of the ceresine bath throughout was never above 140° and was at 127° when distillation was interrupted. The oily distillate was almost transparent like water, had a burning taste and weighed 29.5 g. The boiling point of *dl*-glyceric aldehyde diethyl acetal as given by Wohl[1] is 136° at 27 mm. pressure. The above material was redistilled subsequently and was found to distil freely at 132° at 22 mm. pressure with an outside bath temperature of 140°. The boiling points observed (121° at 11 mm.; 132° at 22 mm.), therefore, coincide very closely with those of *dl*-glyceric aldehyde diethyl acetal as observed by Wohl.[2]

In order to complete the identification of this oil as *dl*-glyceric acetal, it now remained only to show that it yields *dl*-glyceric aldehyde upon hydrolysis. 1.6 g. of the above oil were dissolved in ten parts of 0.1 N sulfuric acid[3] and allowed to stand at room temperature for two days. The mixture was then carefully neutralized with barium hydroxide, filtered and reduced to a thick syrup in a desiccator over sulfuric acid. A few days after stirring with a glass rod the thick syrup showed signs of crystallization, and in about two months assumed the form of an opaque, brittle nearly white, solid mass. When particles of this mass were dissolved in water the solution reduced Fehling's solution within a minute in the cold and gave the characteristic aldehyde test with Schiff's reagent. The taste resembled that of the original acetal of which no doubt a considerable amount was still left unchanged.

A 10 g. portion was similarly hydrolyzed and after concentrating to a syrup *in vacuo*, when treated with ammoniacal lead acetate solution, gave the characteristic precipitate of the lead compound of *dl*-glyceric aldehyde which turned yellow on exposure to the air as described by Wohl and

[1] *Ber*, **33**, 3103 (1900).

[2] In one experiment a considerable quantity of syrup was treated as in (*d*) except that it was allowed to stand in the laboratory instead of in the refrigerator. When worked up I was greatly surprised to obtain about 30 g. of a low-boiling liquid and no *dl*-glyceric aldehyde diethyl acetal whatever. This compound, boiled at 97–100° at 12 mm. or 93–96° at 8 mm. pressure. When it is recalled that experiment (*d*), in which the hydrochloric acid was not neutralized, quickly gave 10 g of a similar low-boiling distillate and that experiment (*e*), in which I took special pains to neutralize quickly, gave none of this low-boiling compound whatever, it seemed clear that the compound is in some way related to glyceric aldehyde. Further experiments will determine whether or not it is, as is suspected, the β-ethyl glucoside of *dl*-glyceric aldehyde.

(Since the above was written Emil Fischer (*Ber*., **46**, 1983) has published a paper on glucosides in which he has expressed the belief that a glucoside of glyceric aldehyde is formed under the conditions here described and in which he has promised to investigate this possibility, so that it will no doubt shortly be known whether an ethyl glucoside of glyceric aldehyde is formed here or not.)

[3] Wohl, *Ber*., **31**, 1800; **33**, 3103.

Neuberg.[1] The original crude material also gave this test. When several drops of a 0.25% solution of this syrup were mixed with 0.5 cc. of a cold saturated solution of phloroglucinol, in the presence of a trace of sulfuric acid, the flocculent precipitate described by Wohl and Neuberg[1] was formed at once when the mixture was immersed in hot water. This syrup also gave the Fehling solution test and the Schiff test described above. The syrup with which these tests were made did not crystallize and had a bitter taste so that it clearly lacked some of the essential characteristics of pure dl-glyceric aldehyde.

These experiments had reached this point when they were interrupted in order to synthesize dl-glyceric aldehyde according to Wohl's method.[2] In the light of the experience gained here, the experiments were then taken up again and completed as described below.

(e) Six hundred grams of the glycerol oxidation syrup, which had been standing in the laboratory for six months, were dissolved in 6 liters of absolute alcohol containing 1% of dry hydrogen chloride and kept in an ammonia-cooled refrigerator for three months. This solution was worked up in three equal portions of 2 liters each as follows: Each portion was treated with 200 cc. of water and then shaken vigorously with an excess of $PbCO_3$ for an hour or more. Finally the last portions of acid were removed by adding small amounts of sodium bicarbonate until the solution was no longer acid to moist litmus paper. This solution was then concentrated in vacuo to a rather thick syrup. About two volumes of water were added in which the syrup was readily dissolved. The whole was now saturated with potassium carbonate. A dark red upper layer separated which was taken up in ether. The remaining solution was then extracted four or five times more with ether. A very thick, almost black, tar remained as the residue of the top layer. The orange colored ether solution was dried with potassium carbonate and concentrated, which gave 125 g. of a red oil. This distilled in vacuo gave 50 g. of a colorless distillate boiling between 100° and 140° at 8 mm. pressure. On redistilling, 37 g., distilling between 108° and 125° (mostly 118° to 122°) at 8 mm. pressure were obtained. This was dissolved in 370 cc. 0.1 N sulfuric acid and allowed to stand at room temperature for one week. Two grams of glacial acetic acid were added and then 170 cc. of 0.212 N barium hydroxide. After filtering off the barium sulfate the solution was adjusted by the addition of small amounts of 0.1 N sulfuric acid until only a slight positive test for barium could be obtained. This solution was freed from barium sulfate by filtering through a filter containing a pinch of washed animal charcoal. The filtrate was freed from water by distilling in vacuo. The yellow gum was taken up in absolute alcohol, treated with ether to

[1] Loc. cit

[2] Cf. This JOURNAL, 36, 1908 (1914).

remove inorganic matter, and concentrated *in vacuo*   The syrup obtained was inoculated with a few particles of crystalline *dl*-glyceric aldehyde.   In a week crystallization was complete   The crystals were filtered off, washed freely with absolute alcohol and dried in the air for one day and then three days *in vacuo* over concentrated sulfuric acid   These crystals melted at 142°   When mixed with *dl* glyceric aldehyde, obtained by Wohl's method and similarly dried, the melting point (142°) was unchanged   A second crop of 1 g made the total quantity obtained 5 g, *i e*, about 25% of the amount theoretically possible if all of the material hydrolyzed was glyceric aldehyde acetal

It was thus definitely established that this oxidation syrup contains *dl* glyceric aldehyde, furthermore, it is also clear from the data given that this method, at least in its present form, is valueless as a practical method of preparing *dl* glyceric aldehyde   Wohl and Neuberg[1] succeeded in converting only 11% of their *dl* glyceric aldehyde into the diethyl acetal when they used the pure sugar   In Experiment (*d*) only 5 1% of the crude material was obtained as the acetal   In another experiment 7 5% was obtained as crude acetal   If these acetals had been absolutely pure this would be a very favorable result, but they were no doubt mixed with small amounts of other acetals or acetal like compounds of glycerol, etc, which either failed to hydrolyze, or form products of hydrolysis which prevent the crystallization of the *dl* glyceric aldehyde present to a large extent   Such acetals and acetal like derivatives of aldehyde with glycerol and the higher alcohols are known to be formed[2] and especially in the presence of hydrogen chloride[3]

The results just presented make it clear that it ought to be possible[4] to obtain crystalline *dl*-glyceric aldehyde directly from the glycerol oxidation syrup by seeding the absolute alcohol solution with the crystallized material   All my efforts in this direction have thus far met with practically negative results   In each test in which it was tried a very small amount crystallized out on long standing, but the amount thus obtained was negligible for practical purposes   The dihydroxyacetone of which there is no doubt some present, and possibly the glycerol appear to hinder crystallization   Further experiments with this syrup are, however, still being made

Summary.

It has been shown that the reaction mixture, obtained on oxidizing

[1] *Loc cit*

[2] Cf Meyer and Jacobson's "Lehrbuch der Org Chemie," I, II, pp 157 and 171 for references

[3] Schultz Tollens, *Ann*, 289, 29 (1895), Nef, *Ibid*, 335, 215 (1904), and Fischer, *Ber*, 28, 1169 (1895)

[4] Cf also the paper on the preparation of glyceric aldehyde according to Wohl's method THIS JOURNAL, 36, 1908 (1914)

glycerol with hydrogen peroxide in the presence of ferrous iron, contains *dl*-glyceric aldehyde:

(1) By converting the aldehyde into glyceric aldehyde diethyl acetal, which was separated by extraction with ether and subsequent distillation and was identified by its color, taste, boiling point, and,

(2) By liberating and crystallizing pure glyceric aldehyde from the syrup obtained on hydrolyzing the above acetal in 0.1 N sulfuric acid.

The presence or absence of glycolaldehyde and dihydroxyacetone was not established by these experiments.

This is the first time that either *dl*-glyceric aldehyde or its acetal have been isolated from an oxidation syrup or in fact from any source, except by the synthetic method devised by Wohl. It is likewise the first time that a sugar has been isolated from a reaction mixture by converting it into the acetal.

CHICAGO, ILL.

NEW BOOKS.

Introduction to Modern Inorganic Chemistry. By J. W. MELLOR, D Sc. 1914 pp. xvi + 657. 8vo. Longmans, Green & Co , London, New York. Price, $1.30.

The earlier and similar work by the same author, "Modern Inorganic Chemistry," 1912, has been reviewed in THIS JOURNAL, **35**, 494. In the preface to the present book the author says: "I have prepared a smaller introductory volume to suit students who want to start with a rather simpler book, and I have been persuaded to introduce some pages dealing with a few of the more important compounds which the inorganic chemist borrows from the organic chemist. My larger book can now be regarded as a kind of sequel to the present work."

We all believe that good teaching requires us to arouse and hold the attention of the student, but those of us who have to perform this task for freshmen may well be discouraged over our feeble efforts on reading such an exciting book as this. Our attempts to keep the students awake by such crude means as strange smells and explosions are here supplanted by poetry and drama. Who ever suspected that chemistry afforded such opportunities for literary effect as we find on page one? "Wind is air in motion, and wind has sufficient energy to propel our sailing ships, to drive the machinery of our windmills, and, when stirred by cyclonic blast, to uproot trees, sweep away buildings, and lash the surface of the ocean into wild monster waves." Again, how the student will be aroused by the paragraph commencing "Let us assume the function of a judge in a law court and sum up the evidence for the jury," etc. How many of us have ever thought of reciting stanzas from Shelley's poem "The Cloud" to enliven our lecture on water? We find a paragraph headed, "Nature Abhors

a Vacuum," and the next, "Death of the Hypothesis· Nature Abhors a Vacuum." There lacks only an illustration of Nature shrinking in terror from a Vacuum, and another of the Dying Hypothesis.

But if the above suggested illustrations are lacking there is no dearth of others. We are shown countless hands holding test tubes, mice languishing in miniature black holes of Calcutta, a man watching a big pile of wood turning to charcoal, bacteria growing on the root of a bean plant, literally dozens of generating flasks with delivery tubes and pneumatic troughs, eyes looking, mouths blowing, and many other unique chemical phenomena. The visual memory is surely not neglected. (One of these illustrations, molecules of hydrogen and chlorine, on page 150, is not arranged according to the labels.)

The author is much interested in words. He distinguishes carefully between the Latin and Greek numeral prefixes, although he allows "trivalent" to slip in, p. 523, instead of his chosen "tervalent." We wonder if beginners in England are usually required to understand such terms as "Fremy's salt," "atmolysis," "eremacausis," "temoin tube," etc.?

A suggestive feature of the book is the unconventional order of presentation. No attempt is made near the beginning to treat completely compounds of any element. The effort seems to have been rather to select only such descriptive material as will aid in presenting the fundamental principles. There are places, however, where one hunts in vain for any sequence. Thus, in Chapter XXIX, we find several paragraphs on air followed by one on "Maximum, Active, and Sleeping Valences." On p. 282 we find a paragraph on "Dialysis" (being a treatment of colloids) out of any apparent connection with the rest of the chapter. (Dialysis is again defined on p. 594.)

There are very full historical references. The student is usually given the historical explanations of phenomena—as, for example, in the full discussion of the phlogiston conflict—before being introduced to the modern viewpoint.

In reading a textbook which is "modern" by title, one is surprised to find no use made of the ionic theory. It is presented in Chapter XXIII, but in terms that indicate that the author is rather afraid of anything so hypothetical. Thus, "The ionic hypothesis is to be regarded as a 'daring stroke of scientific speculation' which is very fashionable;" and later, "In this way the ions have been invested with such imaginary properties as may be needed to keep the ionic hypothesis in accord with the facts. Quite an elaborate system, fairly consistent with itself, has been founded on the above postulates. Neither the ionic nor the chain (Grotthus) hypothesis has proved an adequate explanation of the facts, and although the majority of chemists favor the ionic hypothesis, yet it is recognized

that it has many defects which will render a change necessary when chemists can think of a better." This fear of overbold hypotheses does not prevent the author from confidently writing structural formulas for a large number of inorganic compounds; and explaining that the failure of ammonia to precipitate the hydroxides of magnesium and manganese in the presence of ammonium salts as due to the formation of double salts. It is always interesting to find what theories are accepted without qualm by those who look upon ions with suspicion.

On p. 414 we find the possibility of arranging the elements in a series "representing the strength of the current (in volts)," etc. A sentence on page 458, referring to passive iron, says what the author evidently does not mean.

As in the larger book, numerous questions are subjoined to each chapter. These are exceedingly interesting, and would alone repay the teacher for the purchase of the book.   ·   JOEL H. HILDEBRAND.

Die Theorie der Strahlung und der Quanten. VERHANDLUNGEN AUF EINER VON·℞. SOLVAY EINBERUFENEN ZUSAMMENKUNFT (30 Oktober bis 3 November 1911). Mit einem Anhange über Die Entwicklung der Quanten theorie vom Herbst 1911 bis zum Sommer 1913. In Deutscher Sprache herausgegeben von A Eucken, Halle. Druck und Verlag von Wilhelm Knapp, pp. i–xii und 1–405   Price, 15 M 60 pf.

This volume bears witness not only to the extraordinary activity and success of the German physicists in the development of the Quantum theory, but also to their industry and zeal in getting the latest phases of this subject both from the experimental and the theoretical side into the most convenient possible form for the use of the German scientist. The book before us represents, in the first place, the translation into German of the addresses and discussions on the Theory of Quanta which were held in Brussels in November, 1911, and were published in French in 1913. These addresses represent practically the only source to which one can as yet go for authoritative information as to what is involved in the theory of Quanta and what experimental success that theory has had. If, however, these addresses were the entire content of the volume, one might question whether their translation into German, when they were already available in French, would be worth while, even from the point of view of the German reader. For papers on a subject which is in its early infancy, the aspect of which is changing almost every month, must, of necessity, have much about them which is ephemeral. But Dr. Eucken has done much more than render these notable addresses into good German. He has added a thirty-five page paper of his own which is just as notable as any paper which was presented at the Solvay Congress. In it, Dr. Eucken, though a very young man himself, has sketched, with the hand of a master,

the developments of the Quantum theory from the fall of 1911 to the summer of 1913. There are few men who possess either the ability or the knowledge to present so comprehensive, and at the same time, so judicial and so discriminating a view of all the work which appeared within these two years upon this subject. This review gives to the German edition of the "Theory of Radiation and of Quanta" a value greatly in excess of that possessed by the French edition.

To present a review of the content of the addresses themselves is wholly beyond the possibilities of a book review such as this. There is a limit beyond which *concentration* cannot be carried and this limit was about reached in some of the original addresses. Suffice it to say that anyone who would familiarize himself with the theory of Quanta, can do no better than to get the book in hand and read the papers of Einstein, of Nernst, of Planck, of Lorenz, of Sommerfeld, of Langevin and of Eucken. The paper of Perrin is very long and has no immediate bearing upon the theory of Quanta. Also, the papers of Knudsen and of Jeans may be omitted for the purpose at hand; the first, because it does not bear on the subject of Quanta, and the second, because the viewpoints taken in it have now been abandoned even by the author. All the rest of the volume is a storehouse of ` information for the student of the theory of Quanta.

<div align="right">R. A. MILLIKAN.</div>

Die Lichtbrechung in Gasen als physikalisches und chemisches Problem. DR. STANIS-
   LAW LORIA. Braunschweig. Vieweg & Sohn 1914 pp. vi + 92. Price,
   3 Marks

The "Sammlung Vieweg" is to be devoted to scientific or technical matters which are in active development By means of brief monographs it hopes to make their present state more widely known and to suggest the directions of possible progress.

Dr. Loria's little book is the fourth of the series. The literature concerned with refraction in gases is extensive. Much of it, though still of interest to the historian or bibliographer or student of methodology, is not utilized in this monograph, whose object is to revise all of our experimental knowledge of the refraction and dispersion of light by gases, in the hope of obtaining, in the future, information as to the structure of the atom. Since this subject will interest, not only physicists, but also chemists, the book begins with a chapter for the benefit of the latter, entitled "Elektromagnetische Dispersionstheorien."

The working model of the optical action of even the simplest molecule or atom is not yet devised. This little book well sets forth the facts and theoretic relations from which such a model may sometime be derived. It is commended to the attention of those who are interested in physical chemistry. EDWARD W. MORLEY.

Crystallography. An Outline of the Geometrical Properties of Crystals. By T. L. WALKER, M.A., PH.D. pp. xiv + 204. Illustrated. Cloth, 6 × 9. New York: McGraw-Hill Book Co. 1914. Price, $2.00.

This is the first comprehensive treatment in English of the fundamental concepts of crystallography based on the methods of Victor Goldschmidt. The treatment is practical rather than theoretical. The author lays especial stress in the projection of crystal forms and the derivation of their symbols from the projections.

The book consists of 17 chapters, of which 8 are very short. These are devoted to such subjects as the chemical and physical properties of crystals, their formation, symmetry, the irregularities of crystal surfaces, crystal drawing, etc. Of the remaining 9 chapters, 6 deal with the discussion of the six crystal systems, one treats of crystal aggregates (mainly twinned crystals), one of the mathematical characteristics of crystals, including their measurement and projection and in one—the last—the author illustrates the methods of procedure in crystallographic investigations by reprinting in full the article by Goldschmidt and Nicol on "New Forms of Sperrylite," and that by Eakle on "Colemanite from Southern California." This last chapter serves as a summary of all that precedes it.

The volume is satisfactory in every respect. It is clearly written and well printed; its discussions are logical and the subject matter is fundamental. The book is an excellent one for mature students and for those who are familiar with the elements of crystallography. It is unquestionably the best book in English for those who desire to make a serious study of crystals. Its author and publisher are to be congratulated upon its publication.   W. S. BAYLEY.

Quantitative Analysis. By EDWARD G. MAHIN, PH.D., Associate Professor of Chemistry in Purdue University. First edition. New York: McGraw-Hill Book Company, Inc. 1914. pp. ix + 511; 119 ills. 14 × 20 cm. Price, $3.00 net.

This is another member of the International Chemical Series, of which Prof. H. P. Talbot is consulting editor, and is uniform in external form with the other members of the series.

To quote from the preface, "The author has felt a desire that has probably been felt by every teacher of quantitative analysis, to produce a book that would cover the ground that he wishes to cover in the college courses, providing a reasonable degree of latitude in the selection of exercises for other possible users of the book, and at the same time to present a theoretical and practical discussion of the subject, sufficiently simple to be comprehended by the average student but not so elementary as to destroy his self-respect..... The general discussions have been given a large share of attention although elaborate or involved theoretical discussions have been, as far as possible avoided." The first half of the book is devoted to principles and standard methods of analysis, as may be gleaned

from the titles of Chapters 1 to 10: general principles, gravimetric analysis, experimental gravimetric analysis, electroanalysis, volumetric analysis, color change of indicators, standardization, experimental volumetric analysis, oxidation and reduction, titrations involving the formation of precipitates. Silver chloride, by the way, must fuse far above 151° (p. 70), for it will be recalled that Richards latterly dries it at 250° without fusion. The second half of the book is entirely occupied by Chapter 11, analysis of industrial products and raw materials, with the following sub-heads: carbonate minerals (6 pp.), silicate minerals (7 pp.), coal and coke (total 24 pp.), gas mixtures (18 pp.), burning oils (6 pp.), lubricating oils (5 pp.), edible fats and oils (26 pp.), water for industrial uses (13 pp.), water for sanitary uses (26 pp.), iron and steel (33 pp.), fertilizers (18 pp.), dairy products (23 pp.), assaying gold and silver ores (22 pp.), from which titles one can obtain an indication of how far the author has endeavored to cover some of the fields of applied analysis.

Even in the second part of the book, the manual training solidity of the subject is leavened somewhat by an infusion of reason and reasonableness, and the unavoidable high concentration of facts and directions somewhat diluted by recollections of theory. "References to original papers have been carefully selected with a view to actual reading by the student.. " The book is modern and well-done, and will doubtless prove acceptable to many who wish to use a book of a content such as this one offers.

ALAN W. C. MENZIES.

Quantitative Analysis by Electrolysis. By ALEXANDER CLASSEN with the cooperation of H CLOEREN Translated from the "Thoroughly Revised Fifth German Edition" by William T Hall, Assistant Professor, Massachusetts Institute of Technology. New York John Wiley & Sons, Inc, London· Chapman & Hall, Limited. 1913 8vo. x + 308 pp 52 figures Cloth, $2 50 net (10/6 net)

This book was issued sometime ago, with the excellent print and binding characteristic of the publications of J. Wiley and Sons. As stated in the review of the German edition (THIS JOURNAL, 31, 513) this *fifth* edition differs particularly in its introduction from the previous editions, and is altogether one of the best books on the subject. As before, the book consists of four parts—Part I, Introduction, 100 pages; Part II, Electro-analytical Determinations, 88 pages; Part III, Separation of Metals, 63 pages. and Part IV, Special Analyses, 60 pages. The introduction has been rewritten entirely, and presents the fundamental facts of electro-chemistry according to our present-day manner of viewing them. This presentation is fairly accurate, but the absence of divisional headings and experiments or demonstrations makes it difficult for study by a beginner.

The other parts of the book retain the form and much of the matter of the former editions, but the results of recent investigations on the subject have been carefully added, and obsolete matter has been omitted. The

information given is reliable in the main. It is to be regretted that the author has omitted as important a method as the ammoniacal electrolyte for the determination of silver, and that he credits the cyanide electrolyte for silver as being absolutely accurate; also, that he fails to mention that all methods for determining zinc give too high results. But these errors and omissions are exceptional.

The presentation of the separate topics is excellent, but as a whole the book lacks plan: it does not give the student such a perspective view of the subject as a modern presentation should give. The metals are not pre-sented in their electrochemical relation. Thus in Part II the metals are taken up in this order: copper, lead, cadmium, bismuth, silver, etc., which may be a very good order for a series of exercises to be given to students, but which has absolutely no theoretical basis, and hence is not a desirable order for either a textbook or for a reference book in which facts are to be correlated as much as possible. This lack of correlation shows itself to particular disadvantage in Part III—Separation of Metals--in which, with proper plan and correlation, much needless and really bewildering duplication could have been avoided.

Part IV—Special Analyses—is particularly valuable. It reflects the author's wide experience and great ability in selecting and combining the methods for different metals into plans for the rapid and accurate analysis of special compounds such as the commercial alloys and the important metalliferous minerals.

The book may truly be designated as one of the standards of analytical chemistry, and should be found in every chemical library.

<div align="right">E. P. SCHOCH.</div>

Qualitative Chemical Analysis. A Laboratory Text Treating of the Common Elements and their Compounds. By ANTON VORISEK, Professor of Analytical Chemistry, College of Pharmacy, Columbia University, in the City of New York. P Blakis-tons' Son and Co., Philadelphia. pp. x + 226, with a plate of spectra, tables and text figures   Price, $2.00.

The appearance of still another textbook on Qualitative Analysis can hardly fail to cause some curiosity on the part of teachers regarding the originality of the material contained in the book, and of the method of presentation. The author of this book states in the preface: "The object of the volume is to present a concise but thorough course of qualita-tive analysis of the commonly occurring compounds and their chemical constituents." Many other texts have had the same purpose, and have in a large number of cases fulfilled it with distinct success. It therefore becomes necessary to seek the qualities of this book which mark it as dis-tinct from those we already possess.

The thorough description of all the compounds the student is likely to meet in an elementary course, or even in a more advanced one, is a feature of this

book wanting in nearly all the smaller texts. These descriptions precede the presentation of the systematic separations and are of such a nature that the student who has mastered them is in a position to prepare for himself schemes of analysis. This is true not only of the basic analysis; for the same method is adopted in the presentation of the analysis for acidic constituents. The concise form in which the chemical facts are thus presented should make the book of value as a laboratory reference book.

It is to be regretted that these excellent features are marred by the absence, in all discussions and reactions which accompany the descriptions, of any regard to the theories of ionic dissociation or to the reversibility of reactions developed in other parts of the book. Even though the author accepts the prevailing views of chemistry in aqueous solutions he writes reactions, such as the formation of barium sulfate and silver chloride as, $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$, and $AgNO_3 + HCl = AgCl + HNO_3$, and cites these as *typical examples of irreversible reactions*. (See p. 3 and again p. 185.) Moreover, the theoretical portion itself is weak and inaccurate, and its utility in the correlation of the facts and methods presented is exceedingly slight.

Some of the inaccuracies are of rather a serious nature. The algebraic statement of the mass in equation b on page 180, and its application on page 181 and in other parts of the book, is, to say the least, unintelligible. Again, on page 180, the formula for hydrogen fluoride in aqueous solution is given as HF, whereas it is generally recognized that nearly all the substance present in such a solution has the formula H_2F_2. Similar examples of inaccuracy and vagueness are not infrequent in other parts of the book.

Altogether, the usefulness of the book, from either the scientific or the pedagogical aspect, is by no means apparent. LUDWIG ROSENSTEIN.

Nucleic Acids. Their Chemical Properties and Physiological Conduct By WALTER JONES, Ph D , Professor of Physiological Chemistry in the Johns Hopkins Medical School Longmans, Green and Company, London, 1914 viii + 118 pp , Royal Octavo Price, $1.10.

This small volume, after considering historically the discovery of nucleic acid and its clear separation from the nucleins and nucleoproteins, takes up a detailed discussion of its chemistry. The identity of all animal and of all vegetable nucleic acids is emphasized, after which thymus nucleic acid and yeast nucleic acid are taken up at length as representative members of these groups. The second half of the volume deals with the physiological behavior of nucleic acid.

The book, as a whole, states fairly our present knowledge of the subject. Due consideration is given the several score of workers who have made this field, and their several hundred articles. But it is more than the so common review, in which all findings and all views are given the same space, and are made to appear as of equal value. Jones' view is critical and since

his contributions to the biochemistry of nucleic acid and its derived pur-
ines, and to the ferments acting upon these, are to be counted among the
really substantial ones of American physiology, his judgment means some-
thing.

An appendix to the volume gives in excellent form an outline for pre-
paring thymus nucleic acid, for isolating and identifying its various de-
rivatives and for proving the presence or absence of the various purine
ferments.

One does not add this new volume to the Plimmer and Hopkins series
of monographs on biochemistry without renewed commendation of the
· editorial spirit which has brought them into being, and of the courage of
the publishers in bringing them out. We could, to the benefit of scientific
development in the United States, advantageously exchange many of
our textbooks for monographs of this type. Nor does one note carelessly
that, in adding Jones' name to the list, we become indebted to another
non-medical investigator and writer for light in a field which from many
angles has been considered peculiarly medical. Medical men have literally
filled shelves with books and articles on "uric acid" and its allies and said
nothing. Will the day not come soon when our ranks will again show the
effects of that same mental discipline demanded in other branches of
science? · MARTIN H. FISCHER

THE JOURNAL

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American Chemical Journal
(Founded by Ira Remsen)

A PRELIMINARY STUDY OF THE CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL AT 15°, 25° AND 35°.[1]

BY E P WIGHTMAN J B WIESEL AND HARRY C JONES
Received August 24 1914

Introductory.

Considerable work has been done in this laboratory, especially during the past five years, on the conductivity and dissociation of organic acids in water as a solvent, over a fairly wide range of temperature and dilution This investigation is a continuation of those in non aqueous and mixed solvents, which have been in progress in this laboratory during the past dozen years[2] Since, up to the present but very little has been done here with solutions of the organic acids in absolute ethyl alcohol, it was decided to extend our investigations into this field[3]

A few rather crude measurements of the conductivity of organic acids were made comparatively early in the history of the conductivity method Wakeman,[4] in 1893, measured the conductivities of certain organic acids in mixtures of alcohol and water, ranging from pure water to 50% alcohol He calculated the dissociations of these acids and their dissocia

tion constants. The dissociations decrease slowly with increase in the amount of alcohol present. The constants decrease much more rapidly for the same increase in alcohol. Wakeman plotted curves with molecular conductivities as ordinates and percentage alcohol as abscissas, and showed that, when they were extended beyond 50% alcohol in the direction of 100% alcohol, the conductivities probably approached zero as a limit. He calculated that dissociation in the mixture is much less than would be expected, and showed that the Ostwald dilution law could not be applied to the mixtures containing large amounts of alcohol.
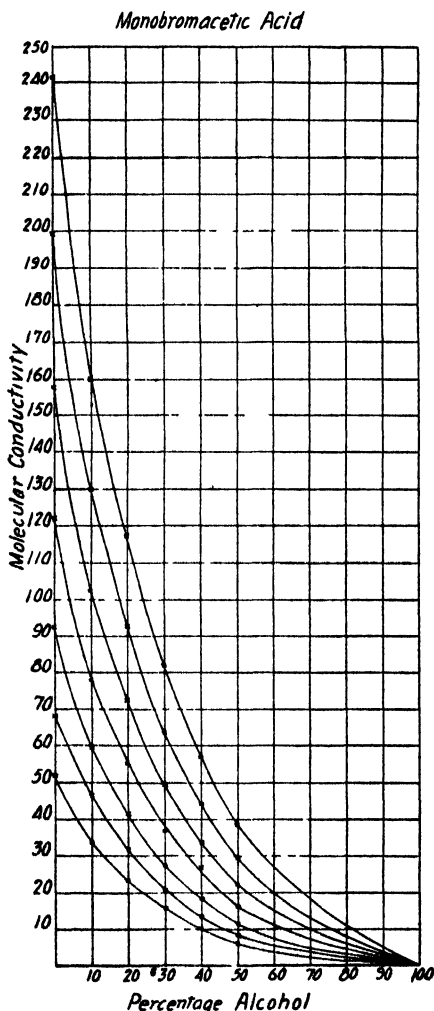
Schall,[1] in 1894, determined the conductivity of certain organic acids in ethyl alcohol, and in mixtures of ethyl alcohol with water. We also did some work on isobutyl alcohol. Schall concluded from his results that the molecular conductivity of organic acids is much less in the alcohols than in water, and that the acids behave very differently in alcohol-water mixtures than in the pure solvents. Some of them seem to behave just the opposite of what might be expected from their conduct in the pure solvents. For example, picric acid gives a much higher, and the others much lower, conductivity values in water-alcohol mixtures than in the pure alcohol.

A careful piece of work on the conductivity of certain organic acids in absolute alcohol at 18° seems to have been done by Wilderman[2] in

Fig I

[1] Z physik. Chem., 14, 701 (1894).

[2] Ibid , 14, 231 (1894).

1894. A great number of precautions were taken by him in preparing the solutions and in measuring the conductivity. He does not give his results with the weaker acids, but simply states that between the volumes 10 and 160 the molecular conductivity increases approximately proportional to the volume. In summing up his work, Wilderman says that it is possible to apply the Kohlrausch method to the determination of the conductivity of strong acids in absolute alcohol, but that no reliable results could be obtained for such weak acids as acetic, monochloroacetic and succinic. He remarks that much time and patience on the part of the experimenter are required to obtain results which are at all reliable.

In a second investigation[1] Wilderman studied the same acids as in the earlier work, using in this case a precision galvanometer method and working at 25° instead of 18°. We found this method more generally applicable than that of Kohlrausch.

Considerable work[2] has recently been done in this laboratory on the conductivity of solutions in both methyl and ethyl alcohols, but this need not be discussed here.

Experimental.

The conductivity apparatus and method used for making the measurements were similar to that employed in previous work in this laboratory, except that on account of the high resistance offered by the alcoholic solutions of the acids, it was necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells has already been described.[3]

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was secured by the combination of a specially devised gas regulator and thermoregulator. These have already been described in earlier papers.[4]

In coöperation with Dr. P. B. Davis, of this laboratory, a new form of constant temperature bath was also designed. Its construction can be seen from Fig. II. A full discussion of the finally adopted form will be presented in a paper to be published by Davis, Putnam and Jones. In these baths the temperature ordinarily does not vary more than o o2° which is sufficiently constant for our purpose. With special precautions as to insulation against changes in temperature, and with further modification of the thermoregulator, the variation can be decreased to a few

[1] Z physik Chem , 14, 247 (1894)
[2] Carnegie Institution of Washington, Publications Nos 80 and 180.
[3] Am. Chem. J., 42, 527 (1909), 44, 64 (1911).
[4] Z. physik. Chem., 85, 519 (1913).

thousandths of a degree. Aside from the better temperature regulation obtained in this form of thermostat bath, there are also one or two other advantages derived from its use. The bath is made of copper which does not rust, and the stirring arrangements and the cooling coil are on the side of the bath, and are therefore out of the way. A number of minor improvements were also made.
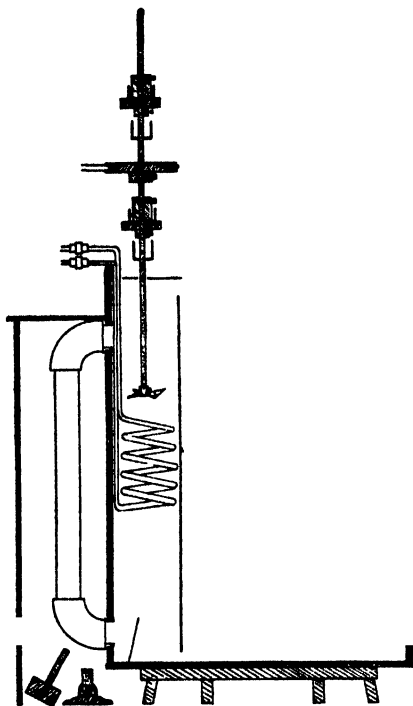
Fig. II.

Solutions were made up in 200 cc. flasks calibrated for 25°, and the measurements of the conductivities of these solutions were made at 15°, 25° and 35°. Pipets, on account of greater convenience in handling, were frequently used for measuring purposes. They were in all cases carefully recalibrated. Corrections for the expansion and contraction of the alcoholic solutions at 35° and 15°, respectively, were of course applied to the conductivity measurements.

The alcohol was prepared by heating ordinary 95% alcohol for several days with fresh lime in a copper tank, provided with a ground brass stopper and reflux condenser, and then distilling it through a block-tin condenser. The distillate was reheated with fresh lime and again distilled, the first and last portions of this distillate being discarded. A few sticks of sodium hydroxide added during the last day of heating insured the removal from the distillate of any aldehyde which might have been present, and which otherwise would have distilled over with the alcohol. By taking proper precautions, it is possible to obtain alcohol by this method having a specific gravity of 0.78506 to within the limit of error ±0.00002. According to Circular 19 of the Bureau of Standards, such alcohol is pure. The alcohol employed in the conductivity measurements varied in specific gravity from 0.78506 to 0.78517, the latter containing 99.964% alcohol. The receiver for the distillate was a 6-liter Jena glass bottle. The stopper was a three-holed paraffined cork. Through one hole passed a siphon, through another an adapter with a glass stopcock, and through the third

a calcium chloride-soda lime tube, also having a glass stopcock. In this way the alcohol was well protected during distillation from impurities in the air, and small quantities sufficient for making up the solutions could be drawn off without exposing the main supply.

After weighing out the quantity of dried and purified acid necessary to make a solution of the required normality, the acid was washed off the watch glass or out of the weighing bottle into a funnel, and then into a 200 cc. Jena flask which had previously been thoroughly washed with water, and then with some of the alcohol with which the solution was to be made up. The flask was then filled to the neck with alcohol and shaken until all the acid had dissolved. It was then hung in a 25° thermostat bath until temperature equilibrium was reached, and finally filled to the mark.

In the meantime a conductivity cell, which had been thoroughly washed the day before, and in which pure alcohol had been allowed to stand over night, was dried with filtered dry air. It was then rinsed several times with portions of the solution which had just been made up, and finally nearly filled with this solution.

It was at first thought advisable to use an alcoholic solution of potassium hydroxide for titration purposes. General difficulties were, however, encountered. An approximately o 1 N solution of potassium hydroxide in absolute alcohol was made up and allowed to stand for a couple of days. The carbonate settles, leaving a clear, supernatant solution. But if the bottle was opened even for a very short time, the solution became cloudy, and when poured into a buret became white with precipitated carbonate.

A method of filtering the solution, being a modification of one previously used in this laboratory, was then adopted, together with an arrangement for siphoning the solu-
tion out of the bot-
tle into the buret.
Fig. III shows the
design of the filter-
ing apparatus. The
t o w e r T con-
tains sticks of so-
d i u m hydroxide,
and T' is partly
filled with metallic
s o d i u m . T h e
former acts as a
protecting agent to
the latter, which
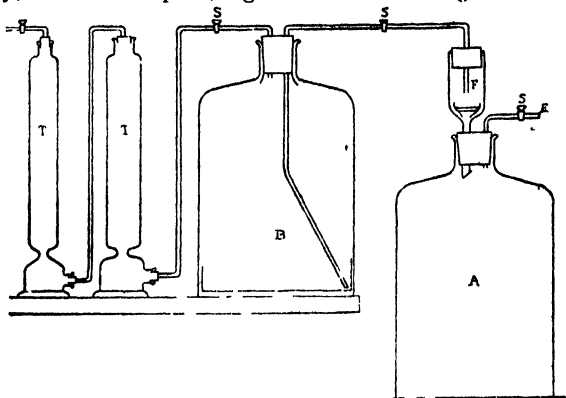
Fig. III.

serves both for removing the last traces of carbon dioxide and for drying the air. B is an empty bottle, which is later interchanged with a bottle filled with an alcoholic solution of potassium hydroxide prepared from freshly distilled alcohol. Tube E is connected with suction, so that dried, purified air passes through the whole system, including the Gooch funnel F, containing asbestos previously washed with an alcoholic solution of potassium hydroxide and then pure alcohol, and through the receiving bottle A. When the system has been thoroughly cleansed with dry air, free from carbon dioxide, the stopcocks G are closed and the bottle B is replaced by the one containing alcoholic potash. The stopcocks are then opened and .suction again applied at E. When all the solution has been filtered, A is removed and, as quickly as possible, the stopper arranged to connect it by a siphon with the buret is introduced as shown in Fig. IV. A little carbonate is formed by opening in this way to the air, but it is a very small quantity, and in the course of a few days is entirely precipitated to the bottom of the bottle.
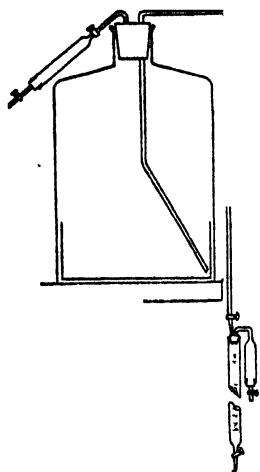
The drying flasks are filled with a mixture of calcium chloride and soda lime, to protect the alcoholic solution when the stopcocks S and S' are opened. The stoppers T and T' are of cork and are thoroughly paraffined. Such a system as this remains protected from the air for a period of several months.

Fig. IV.

The alcoholic solution, in course of time, becomes colored slightly yellow, but its alkaline concentration is apparently not changed, as can be seen by comparing titrations made against a standard acid in February and again in May.

On February 25, 10 cc. of standard acid = 8.87 cc. of alkali.
On May 7, 10 cc. of standard acid = 8.87 cc. of alkali.

The bottle containing the alkali was covered with a dark material, since, in the presence of light, the tendency of the alkaline solution to become colored is much greater than in the dark.

One of the greatest difficulties encountered in connection with the alcoholic potash method was that of temperature changes. The coefficient of expansion of alcohol is so large that even small changes in the temperature of the laboratory and consequent changes in the temperature of the solution will change quite appreciably the normality of the alkali.

It was this difficulty which led us to use an aqueous solution of ammonia with coralline as an indicator, instead of the alcoholic caustic potash

with phenolphthalein as the indicator The ammonia was prepared by heating concentrated ammonia and passing the gas which was given off, first over sticks of sodium hydroxide, which collected a large part of the water vapor and any carbon dioxide, and then over sodium, which absorbed the remainder of the water vapor, and finally into a weighed quantity of conductivity water in a measuring flask, until the amount of the gas necessary to make a o 1 N solution wa dissolved. This solution was titrated against standard sulfuric acid to obtain its normality

Coralline was used as the indicator, because it is sensitive to the organic acids, and is not sensitive to carbon dioxide, except when the latter is present in fairly large quantity In order to test whether coralline is sensitive to small quantities of carbon dioxide, under the conditions under which we worked, another investigator in this laboratory—Mr J E L Holmes—measured out two equal quantities of a standard acid, added an equal amount of coralline to each, and then allowed carbon dioxide to bubble through one of these solutions for some minutes Titrations of both solutions were made, and practically no effect due to the presence of carbon dioxide was found Equal volumes of the standard acid were again measured out and carbon dioxide passed into one of the solutions for a considerable time The two solutions were then titrated There was, under these conditions, a small difference noted In both cases the amount of carbon dioxide dissolved in the solutions was incomparably greater than would ordinarily be present in such solutions as we were titrating It was found necessary to use from eight to ten drops of the solution of coralline in alcohol for each titration Even then the end point is not quite as sharp and distinct as with phenolphthalein

It was found that, when calculating the concentration of the organic acid in the alcohol from the values obtained by titrating against ammonia, a slightly different value for the concentration was obtained from that formed from titrations against alcoholic caustic potash We decided to find, if possible, the cause of this discrepancy, and to apply any necessary corrections A known quantity of the standard sulfuric acid was titrated against alcoholic potassium hydroxide, using phenolphthalein as the indicator Several titrations were made in every case, and then an equal quantity of the acid was titrated against the base, using coralline as the indicator The results in the latter case did not agree with those in the former by about o 2 cc , 10 cc of acid being used in each case That the difference was not due to carbon dioxide, which might have been dissolved in the sulfuric acid, can be seen from the fact that the same difference appeared in the titrations with an organic acid dissolved in absolute alcohol in which carbon dioxide is only slightly soluble

It was found that if the same quantity of phenolphthalein or coralline

used when making the ordinary titrations were added either to pure alcohol or to water, and if these solutions of the indicators alone were titrated against the alkali, and then back against the standard acid, an appreciable quantity of the alkali was required to change the color in the one direction, and about as much of the standard acid to change it in the reverse direction, the alkali and acid being of very nearly the same strength. Corrections for the amounts of alkali and acid necessary to produce such color changes were then applied to the titration volumes of the sulfuric acid and alcoholic potash, when agreement to within the limits of experimental error between the results for the two indicators was obtained. In all of the titrations in which alcoholic potassium hydroxide was used, the temperature of the solution was recorded; and when different from $25°$, which was chosen as the standard temperature, a volume correction was applied. It was found necessary to keep all of the other solutions, particularly those of the organic acids in alcohol, as well as the alcoholic potash, at the standard temperature, and this was not difficult to do.

The titration values of the ammonia and standard acid were also corrected, as just stated, for the amounts necessary to produce color change, and the concentration of the ammonia was then calculated. The normality of 1-2-4 dinitrobenzoic acid in alcohol was determined from this standardized ammonia, making the same corrections as above, and it agreed to within o 2% with that obtained by means of potassium hydroxide. Similar corrections were therefore applied to the titrations of all the organic acids. The sulfuric acid used to standardize the alkali was made up in large quantity, and its normality determined by the usual barium sulfate method.

Owing to the large amount of preliminary work required, it has been possible, up to the present, to make conductivity measurements of only nine organic acids. The same methods of purifying the acids were employed as when the conductivities of these acids were determined in aqueous solution. In most cases the various dilutions were made up by directly weighing the acid.

In the work in alcohol it was necessary to discard all of the weaker organic acids, notwithstanding the fact that our cell constants were about eight times smaller than those of Wilderman. After trying acetic acid several times we gave up hope of obtaining satisfactory results with such weak acids. Even the strongest acids with which we worked do not give a molecular conductivity greater than unity.

Titrations of the acids against the standard alkali were made simultaneously with the conductivity measurements at every temperature. At first the alcoholic solution of the acid was not kept at constant temperature, but it was soon found that, in order to obtain comparative results, and to avoid the considerable fluctuations of laboratory tempera-

ture, it was necessary to have all the solutions continuously at one temperature, preferably at 25°.

Results.

In the following tables of conductivity, V_m is the volume for which the solutions were made up, V_c is the corrected volume. The corrections applied were both for expansion or contraction of the alcohol, and for change in the concentration of the acid due to formation of ester. Molecular conductivity, M_v, was calculated in the usual manner, as were also temperature coefficients and percentage temperature coefficients.

TABLE I MALONIC ACID

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15-25° | | 25-35° | |
Vm	Vc	μv 15°	Vc	μv 25°	Vc	μv 35°	Cond units	Per cent	Cond units	Per cent
8	8 12	0 0190	8 13	0 0237	8 18	0 0319	0 0046	24 5	0 0079	33 9
32	32 9	0 0434	33 2	0 0555	33 7	0 0737	0 0113	26 7	0 0192	35 9
128	129 3	0 0775	129 5	0 0985	129 6	0 1351	0 0207	26 1	0 0359	36 9
512	512 8	0 2533	514 9	0 3160	518 1	0 4335	0 0613	24 2	0 1145	36 4

Specific conductivity of alcohol at 15, 0 000254 to 0 000246 at 25, 0 000257 to 0 000249

TABLE II – o CHLOROBENZOIC ACID

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15-25° | | 25-35° | |
Vm	Vc	μv 15°	Vc	μv 25°	Vc	μv 35°	Cond units	Per cent	Cond units	Per cent.
8	8 14	0 01303	8 16	0 0159	8 28	0 0197	0 00281	21 1	0 00344	22 1
32	33 1	0 01530	33 6	0 0198	34 9	0 0271	0 00451	28 1	0 00605	31 9
128	129 5	0 0279	129 7	0 0371	129 8	0 0555	0 00903	32 8	0 0180	49 2
512	313 8	0 1330	516 5	0 1714	519 9	0 2497	0 0375	20 8	0 0759	44 6

Specific conductivity of alcohol at 15°, 0 000531 to 0 000540, at 25°, 0 000578 to 0 000622, at 35°, 0 000637 to 0 000711

TABLE III – p CHLOROBENZOIC ACID

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15–25° | | 25–35° | |
Vm	Vc	μv 15°	Vc	μv 25°	Vc	μv 35°	Cond units	Per cent	Cond units	Per cent
8	10 0	0 0017	10 08	0 0025	10 11	0 0035	0 00067	48 2	0 00086	41 7
32	33 69	0 0082	34 18	0 0117	34 9	0 0160	0 00315	40 2	0 00382	34 7
128	129 7	0 0157	130 3	0 0189	130 9	0 0270	0 00314	19 9	0 0079	42 4
512	514 8	0 1263	520 0	0 1547	522 7	0 1853	0 0368	29 3	0 0293	19 2

Specific conductivity of alcohol at 15°, 0 000585 to 0 000586, at 25°, 0 000650 to 0 000656, at 35°, 0 000752 to 0 000827

TABLE IV —p-Bromobenzoic Acid

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15–25° | | 25–35° | |
V_m	V_c	$μ_v$ 15°	V_c	$μ_v$ 25°	V_c	$μ_v$ 35°	Cond units	Per cent	Cond units	Per cent
8	8 147	0 00264	8 24	0 00353	8 27	0 0047	0 0008	30 7	0 0012	34 9
32	32 57	0 01252	33 3	0 0147	34 33	0 0200	0 0019	15 4	0 0046	32 3
128	129 1	0 0349	129 2	0 0418	129 5	0 0559	0 0068	19 6	0 0138	33 3
512	512 8	0 1651	517 5	0 1976	518 9	0 2637	0 0307	18 6	0 0607	29 9

Specific conductivity of alcohol at 15° 0 000217 to 0 000214, at 35°, 0 000264 to 0 000233

TABLE V —o Nitrobenzoic Acid

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15–25° | | 25–35° | |
V_m	V_c	$μ_v$ 15°	V_c	$μ_v$ 25°	V_c	$μ_v$ 35°	Cond units	Per cent	Cond units	Per cent
8	8 21	0 00785	8 27	0 00937	8 27	0 0120	0 00142	18 56	0 0025	27 45
32	33 19	0 0204	34 3	0 0253	34 95	0 0337	0 0040	20 31	0 0084	35 44
128	129 3	0 0460	129 5	0 0477	129 6	0 0734	0 0642	35 94	0 0413	17 00
512	512 5	0 1788	517 0	0 2452	518 5	0 2877				

Specific conductivity of alcohol at 15°, 0 000232 to 0 000227, at 25° 0 000242 to 0 000238, at 35°, 0 000237 to 0 000232

TABLE VI —p Nitrobenzoic Acid

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15–25° | | 25–35° | |
V_m	V_c	$μ_v$ 15°	V_c	$μ_v$ 25°	V_c	$μ_v$ 35°	Cond units	Per cent	Cond units	Per cent
32	32 96	0 0102	33 61	0 0151	34 56	0 0214	0 0045	45 5	0 0055	38 2
128	129 2	0 0516	129 3	0 0570	129 5	0 0785	0 0053	12 9	0 0212	37 5
512	512 8	0 1417	517 6	0 1814	520 5	0 2399	0 0401	28 6	0 0565	31 4

Specific conductivity of alcohol at 15° 0 000237 to 0 000231 at 25°, 0 000237 to 0 000227 at 35°, 0 000232 to 0 000216

TABLE VII —1 2,4-Dinitrobenzoic Acid

| | Molecular Conductivity | | | | | | Temperature Coefficients of Conductivity | | | |
| | | | | | | | 15 25° | | 25–35° | |
V_m	V_c	$μ_v$ 15°	V_c	$μ_v$ 25°	V_c	$μ_v$ 35°	Cond units	Per cent	Cond units	Per cent
8	8 13	0 0379	8 24	0 0481	8 24	0 05879	0 0094	25 2	0 0104	22 3
32	33 62	0 9964	33 62	0 0848	33 62	0 10512	0 0171	26 9	0 0194	23 9
128	133 5	0 2556	133 5	0 1670	133 5	0 20043	0 0323	25 3	0 0359	22 4

Specific conductivity of alcohol at 15°, 0 000882 to 0 000936, at 25°, 0 000991 to 0 000935, at 35°, 0 001133 to 0 00123

TABLE VIII —I 2 4 DIHYDROXYBENZOIC ACID

	Molecular Conductivity						Temperature Coefficients of Conductivity			
							15 25°		25 35°	
V_m	V_c	μ_v 15°	V_c	μ_v 25°	V_c	μ_t 35°	Cond units	Per cent	Cond units	Per cent
8	9 99	0 0080	10 06	0 0098	10 10	0 0126	0 0014	20 9	0 0023	28 3
32	33 0	0 0155	33 01	0 0197	33 01	0 0254	0 004	26 5	0 0054	28 3
128	129 1	0 0171	129 3	0 0272	129 6	0 0391	0 100	59 1	0 0117	43 4
512	514 9	0 1008	517 5	0 1464	520 2	0 2018	0 044	44 3	0 0539	37 2

Specific conductivity of alcohol at 15° 0 000551 to 0 000613 at 25° 0 000631 to 0 000682, at 35° 0 000735 to 0 000791

TABLE IX —TETRACHLOROPHTHALIC ACID

	Molecular Conductivity						Temperature Coefficients of Conductivity			
							15 25°		25 35°	
V_m	V_c	μ_v 15°	V_c	μ_v 25°	V_c	μ_t 35°	Cond units	Per cent	Cond unit	Per cent
16	16 08	0 0543	16 21	0 0639	16 21	0 0770	0 0045	16 9	0 0064	18 9
64	64 06	0 1011	64 06	0 1198	64 06	0 1461	0 0093	18 5	0131	21 9
256	258 9	0 1294	259 3	0 1541	260 0	0 1813	0 0121	18 1	0 0171	22 5
512										
1024	1027 0	0 3208	1036 0	0 3860	1043 0	0 4960	0 0309	19 3	0 0527	27 6

Specific conductivity of alcohol at 15° 0 000543 to 0 000554 at 25° 0 000616 to 0 000637 at 35° 0 000711 to 0 000742

The rate at which the organic acids combine with alcohol can be seen from the following data The times at which the titrations were made are given, and the percentage decrease in normality shows the rate of ester formation.

TABLE X —MALONIC ACID

Changes in Concentration

Time	Observed normality	Calculated normality	Per cent decrease in normality
12 40 P M	0 1232	0 1250	1 44
2 30 P M	0 1229	0 1250	1 68
4 00 P M	0 1222	0 1250	2 24
12 50 P M	0 03039	0 03125	2 75
2 30 P M	0 03008	0 03125	3 75
4 10 P M	0 02966	0 03125	5 09
12 00 M	0 00773	0 007812	1 05
2 30 P M	0 00772	0 007812	1 18
4 00 P M	0 00771	0 007812	1 31
12 10 P M	0 001950	0 001953	0 16
2 40 P M	0 001942	0 001953	0 51
4 10 P M	0 001930	0 001953	1 18

TABLE XI

o-CHLOROBENZOIC ACID   p-CHLOROBENZOIC ACID

Changes in Concentration

Time	Observed normality	Calculated normality	Per cent decrease in normality		Time	Observed normality	Calculated normality	Per cent decrease in normality
10 00 A M	0 1228	0 1250	1 76		12 30 P M	0 0996	0 1250	20 32
12 15 P M	0 1225	0 1250	2 00		2 00 P M	0 09919	0 1250	20 65
4 15 P M	0 1210	0 1250	3 20		4 15 P M	0 0989	0 1250	20 90
4 40 P M	0 1208	0 1250	3 36		12 40 P M	0 0297	0 03125	5 09
11 00 A M	0 03018	0 03125	3 43		2 00 P M	0 0292	0 03125	6 40
11 50 A M	0 02976	0 03125	4 77		4 30 P M	0 0286	0 03125	8 42
3 30 P M	0 02914	0 03125	6 76		12 30 P M	0 00771	0 007812	1 31
4 30 P M	0 02862	0 03125	8 42		2 20 P M	0 007691	0 007812	1 55
11 40 A M	0 00772	0 007812	1 18	2 days later	3 30 P M	0 00767	0 007812	1 77
12 30 P M	0 00771	0 007812	1 31		4 10 P M	0 00766	0 007812	1 99
2 30 P M	0 00770	0 007812	1 44		5 00 P M	0 00763	0 007812	2 25
4 00 P M	0 00769	0 007812	1 57		12 35 P M	0 001942	0 001953	0 57
11 35 A M	0 001946	0 001953	0 36		3 15 P M	0 001923	0 001953	1 54
12 30 P M	0 001936	0 001953	0 88	2 days later	12 30 P M	0 001916	0 001953	1 97
2 50 P M	0 001932	0 001953	1 08		3 30 P M	0 001913	0 001953	2 05
4 45 P M	0 001923	0 001953	1 54		4 15 P M	0 001903	0 001953	2 57

TABLE XII

p-BROMOBENZOIC ACID   o-NITROBENZOIC ACID.

Changes in Concentration.

Time.	Observed normality.	Calculated normality	Per cent decrease in normality		Time	Observed normality.	Calculated normality	Per cent decrease in normality
11 30 A M	0 12275	0 1250	1 80		12 15 P M.	0 12176	0 1250	2 60
2 45 P M	0 12129	0 1250	2 97		12 30 P M	0 12088	0 1250	3 30
4 40 P M	0 12088	0 1250	3 30		4 30 P M	0 12088	0 1250	3 30
11 40 A M	0 03070	0 03125	1 76		12 30 P M	0 03013	0 03125	3 59
2 50 P M	0 03007	0 03125	3 76		2 30 P M	0 02914	0 03125	6 77
4 50 P M	0 02914	0 03125	6 76		4 30 P M	0 0286	0 03125	8 45
11 00 A M	0 00774	0 00781	0 89		12 00 M	0 00773	0 00781	1 03
12 15 P M	0 00773	0 00781	1 00		2 30 P M	0 00772	0 00781	1 17
4 00 P M	0 00771	0 00781	1 22		4 00 P M	0 00771	0 00781	1 29
11 10 A M	0 001950	0 001953	0 16		12 10 P M	0 001951	0 001953	0 11
12 25 P M	0 001932	0 001953	1 08		2 40 P M	0 001934	0 001953	0 96
4 10 P M	0 001927	0 001953	1 34		4 10 P M	0 001928	0 001953	1 28

· TABLE XIII

p-NITROBENZOIC ACID   1,2,4-DINITROBENZOIC ACID

Changes in Concentration

Time	Observed normality	Calculated normality	Per cent. decrease in normality	Time	Observed normality	Calculated normality	Per cent decrease in normality
12 00 M	0 03034	0 03125	2 93	12 30 P M	0 1230	0 1250	1 60
2 30 P M	0 02976	0 03125	4 77	2 30 P M	0 1213	0 1250	2 96
4 45 P M	0 02893	0 03125	7 43	4 30 P M	0 1213	0 1250	2 96
12 00 M	0 007738	0 007812	0 95	12 20 P M	0 02974	0 03125	4 83
2 30 P M	0 007734	0 007812	1 00	4 00 P M	0 02974	0 03125	4 83
4 45 P M	0 007721	0 007812	1 17	5 00 P M	0 02974	0 03125	4 83
12 00 M	0 001950	0 001953	0 16	12 35 P M	0 00749	0 007812	4 13
2 30 P M	0 001932	0 001953	1 08	2 30 P M	0 00749	0 007812	4 13
4 30 P M	0 001921	0 001953	1 64	1 day later 10 00 A M	0 00764	0 007812	2 21

This titration was made with the solution after it had stood in the cell over night.

TABLE XIV

1,2,4 DIHYDROXYBENZOIC ACID.   TETRACHLOROPHTHALIC ACID.

Changes in Concentration

Time	Observed normality	Calculated normality	Per cent decrease in normality	Time	Observed normality	Calculated normality	Per cent decrease in normality
11 15 A M	0 10008	0 1250	19 94	11 50 A M	0 06218	0 0625	0 52
12 30 P M	0 09940	0 1250	20 50	12 50 P M	0 06168	0 0625	1 32
2 30 P M	0 09899	0 1250	20 82	3 20 P M	0 06168	0 0625	1 32
4 30 P M	0 09873	0 1250	21 02	4 30 P M	0 06168	0 0625	1 32
12 25 P M	0 03034	0 03125	3 09	12 00 M	0 04561	0 01566	0 32
12 45 P M	0 03029	0 03125	3 09	1 00 P M	0 04561	0 01566	0 32
2 30 P M	0 03029	0 03125	3 09	3 30 P M	0 04561	0 01566	0 32
4 30 P M	0 03013	0 03125	3 59	4 30 P M	0 04561	0 01566	0 32
12 00 M	0 00774	0 007812	0 89	12 15 P M	0 00386	0 00391	1 08
2 30 P M	0 00773	0 007812	1 03	2 00 P M	0 00385	0 00391	1 28
4 15 P M	0 00771	0 007812	1 27	4 00 P M	0 00384	0 00391	1 54
12 10 P M	0 00194	0 001953	0 51	12 25 P M	0 000973	0 000976	0 31
2 40 P M	0 00193	0 001953	1 68	2 10 P M	0 000965	0 000976	1 13
4 30 P M	0 00192	0 001953	1 59	4 10 P M	0 000958	0 000976	1.85

Discussion of the Results.

It will be noted in the above tables that 1,2,4-dinitrobenzoic acid shows an irregularity in its titration values. The conductivity of this acid was determined before we began to keep the solutions used in titration at a constant temperature. In the case of all the other acids the results show that with increase in time a greater amount of esterification has taken place; that is, the normality of the acid has become less. The amount of ester formed in a given time depends upon the nature of the acid.

Since each dilution was made up independently of the others, that is, by direct weight, it is interesting to note that the proportion of ester formed in the less dilute solutions, is much greater than in the more dilute

solutions. Indeed, in some cases there is practically no ester formed in the $N/128$ and $N/512$ solutions. As has already been stated none of the conductivities is greater than unity, and consequently, the molecular conductivity of the alcohol for each dilution is relatively quite large, the correction for this factor being in some cases as much as 70% of the total conductivity. It can be seen from the tables that the conductivity of the alcohol alone varies considerably, usually increasing appreciably with time. Some of the conductivities of the alcohol increase with rise in temperature, some actually decrease, while others remain very nearly constant. We can offer no explanation for this lack of uniform variation, except to call attention to the several factors which might affect the conductivity of the pure solvent. One might be the absorption by the alcohol of traces of various gases or water-vapor from the atmosphere. This, however, ought to be a negligible factor, since our cells were very nearly filled, and were tightly closed with ground-glass stoppers. The decomposition effects brought about by the platinum electrodes may be an important factor. Compare here the work of Wilderman and others on this question. It is evident that the electrodes do have some effect, since fresh alcohol just taken from the bottle does have a fairly uniform conductivity. Part of the effect, with alcohol which stood in the cell over night, might be due to the solubility of the glass cell. This, however, is not at all probable, since our cells have been in constant use in this laboratory for several years, and hard glass is only very slightly soluble in alcohol.
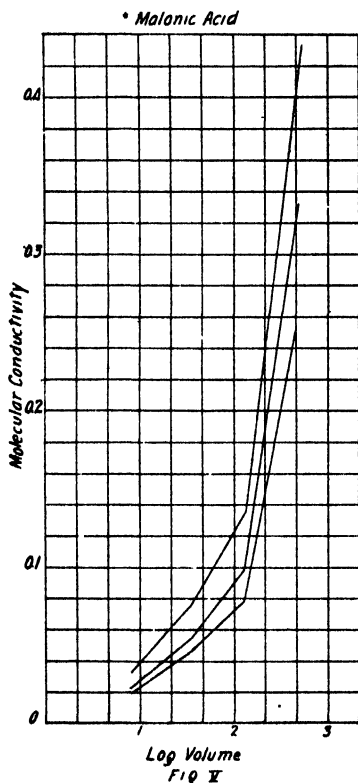
• Malonic Acid

Molecular Conductivity

Log Volume

Fig I

The conductivities of some of the solutions, and curiously enough of the more dilute solutions, vary to a much smaller extent with time, than does the conductivity of the pure alcohol.

It will be recalled that Wakeman plotted curves of conductivity of the organic acids against percentage alcohol (see Fig. I) and on extending the curves in the direction of 100% alcohol they apparently approached

zero conductivity as a limit. As can be seen from our results, the conductivities do not actually approach zero, but a number less and usually very much less than unity.

One of the most interesting facts which came out in this work is the extraordinarily large percentage temperature coefficients of conductivity of the organic acids in alcohol. These range from fifteen to fifty per cent.

There is often a rapid increase in the conductivity of the organic acids with increase in dilution, yet certain of the acids behave in just the opposite manner; e. g., o-chlorobenzoic acid and p-nitrobenzoic acid.

Our results seem to suggest the following possibilities, if we take into account the work done here on the organic acids in aqueous solutions:[1] that there is much greater alcoholation than hydration, and this is decreased with rise in temperature. The work already done in this laboratory renders this highly improbable. The alcoholates may be more unstable with rise in temperature than the hydrates; but water seems to have, in general, far more power to combine with dissolved substances than alcohol.

If dissociation in alcoholic solutions increased with rise in temperature, it might account for the large temperature coefficients of conductivity in such solutions, but this again seems highly improbable.

The greater expansion of the alcohol with rise in temperature would allow a freer movement of the ions, and this is doubtless of some significance. A method for determining the dissociation of the organic acids in alcohol, somewhat similar to that used with aqueous solutions, will, it is hoped, be worked out in the investigation of this subject which is to follow this preliminary one. It will involve the study, in alcohol, of the conductivity

p- Chlorobenzoic Acid

Molecular Conductivity

Log Volume

Fig. VI
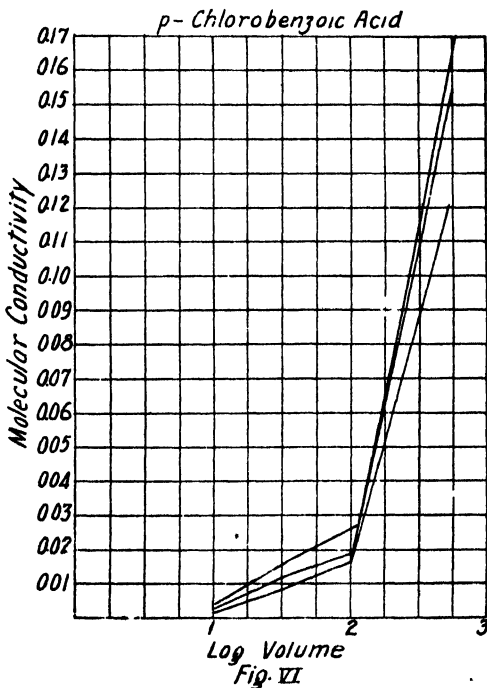
[1] Carnegie Institution of Washington, Publication No 170.

of some salts of the acids, as well as of hydrochloric acid and the chlorides corresponding to these salts.
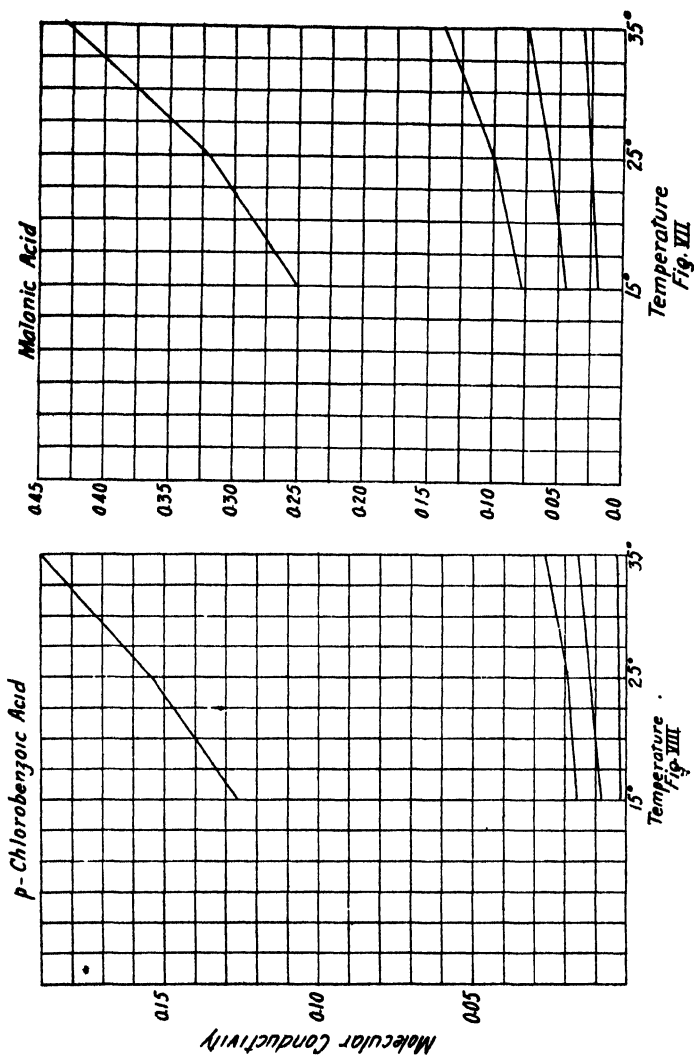
The increase in conductivity with increase in volume is shown graphically in Figs. V and VI. The increase in conductivity with rise in temperature can be seen from Figs. VII and VIII. In the latter case the curves have very much the appearance of those in aqueous solutions. This suggests the

thought that perhaps the increase in molecular conductivity in alcohol with rise in temperature, is a parabolic function, as in aqueous solutions, and that the Euler equation

$$\mu v = \mu o + \alpha t + \mu t^2$$

applies to both

This will be tested in the later work by determining the conductivities of some of the acids at temperatures other than the three already named, and comparing the results obtained, with those calculated from this equation. The most striking feature of the conductivities of the organic acids in alcohol, as compared with the conductivities of the same acids in water, is *their very small value*. When we consider the relative powers of alcohol and water to dissociate salts, the above fact does not at present seem to admit of any very satisfactory explanation. Alcohol has from one fourth to one fifth the dissociating power of water as shown by their dissociation of salts. With the organic acids the conductivities in alcohol are often several hundred times smaller than in water. It is hoped that the further work which is now in progress in this laboratory on this problem may throw some light on this relation.

JOHNS HOPKINS UNIVERSITY
BALTIMORE MD

THE FREE ENERGY OF IODINE COMPOUNDS.

BY GILBERT N LEWIS AND MERLE RANDALL

Elementary Iodine.

The elementary forms of iodine which we shall consider are solid and liquid iodine, I_2 in aqueous solution, and the two gaseous modifications, I_2 and I. Solid iodine is taken as the standard state.

$I(s) = I(l)$ —The free energy of liquid iodine is obtained directly from the melting point of solid iodine, which was found by Ramsay and Young[1] to be $114°$, a value which is in good agreement with those given by Regnault and by Stas. From the vapor pressure measurements of Ramsay and Young the heat of vaporization of liquid iodine has been calculated by Baxter, Hickey and Holmes[2] and shown to be 5250 cal per g atom. From their own measurements which we shall presently discuss more fully, the heat of sublimation of $I(s)$ at the same temperature, $114°$, is 7270 cal. Subtracting, we find in round numbers for our reaction[3] $\Delta H = 2000$ cal

[1] Ramsay and Young *J Chem Soc* **49**, 453 (1886)

[2] Baxter Hickey and Holmes THIS JOURNAL **29**, 127 (1907)

[4] Favre and Silbermann obtained the value 1500 cal but only made one determination

We have no safe means of estimating the heat capacity of liquid iodine. We will therefore write $\Delta\Gamma = 0$. This assumption may be quite erroneous and therefore we must not attempt to use over too wide a range of temperature, the free energy equation[1] which we thus obtain, namely,

$$I(s) = I(l); \quad \Delta F^\circ = 2000 - 5.17T, \tag{1}$$

where the value $I = -5.17$ is found directly by writing $\Delta F^\circ = 0$ at $114°C$. Hence, $\Delta F^\circ_{298} = 460$.

$2I(s) = I_2(g)$.—The heat capacity, per gram atom, of $I(s)$ was found by Nernst, Koref, and Lindemann[2] to be 6.6 at room temperature. The value will doubtless be higher at higher temperatures, but we have no data upon which to determine the temperature coefficient above room temperature. We shall therefore treat Cp as constant. The value of Cp for the gas I_2 we have given in another place[3] as

$$Cp(I_2) = 6.5 + 0.0040T.$$

We thus find[4] for the reaction in question

$$\Delta\Gamma = -6.7 + 0.0040T. \tag{2}$$

The heat of sublimation was calculated by Baxter, Hickey and Holmes[5] to be about 15100 cal. at 30°, whence $\Delta H_0 = 16900$ and

$$\Delta F^\circ = 16900 + 6.7T \ln T - 0.0020T^2 - 78.73T \tag{3}$$

where the value of $I = -78.73$ is calculated from the vapor pressure measurements of Baxter, Hickey and Holmes, who find the vapor pressure

[1] For a discussion of the general form of the free energy equation see Lewis, THIS JOURNAL, **35**, 1 (1913).

[2] Nernst, Koref and Lindemann, *Sitz. Kgl. preuss. Akad Wiss*, **12**, **13**, 261–282 (1910).

[3] Lewis and Randall, THIS JOURNAL, **34**, 1128 (1912).

[4] It may at first sight seem absurd to introduce into Equation 2 a term involving the change in specific heat of I_2 with the temperature when we have neglected a similar term, possibly greater than this, in the heat capacity of solid iodine   This is, however, by no means the case.   In the handling of free energy equations it proves to be as important to use consistent values as to use true ones, and any attempt to round off in the course of a calculation data which have previously been decided upon leads to the utmost confusion   The reason for this will become obvious if we consider a simple example   Suppose that we know accurately the heat capacities of the gases I_2 and I, while the heat capacity of $I(s)$ is not accurately known   Since, however, $I(s)$ is taken as the standard form, the free energy equations to be considered are those corresponding to the two reactions, $2I(s) = I_2(g)$ and $I(s) = I(g)$.   No matter how inaccurate the thermal data may be which are used for $I(s)$, if we use these values consistently and have kept in our equations the accurate equations for I_2 and I, then by subtracting the two free energy equations we will have an exact equation for the reaction $I_2 = 2I$ It is therefore of the highest importance that when values of $\Delta\Gamma$ or ΔH or the constant I are once adopted for one reaction that the data on which these values are based be used in exactly the same form in all other equations   In our first free energy calculations an immense amount of time was lost through neglect of this principle.

[5] Baxter, Hickey and Holmes, *loc. cit*

to be 0.305 mm. at 25° and 2.154 mm. at 50°. Whence, assuming that the vapor obeys the gas law, $\Delta F°_{298} = 4630$ and $\Delta F°_{323} = 3770$ cal. These lead respectively to the values $-78\ 76$ and $-78\ 71$ for I. We will take $I = -78.73$ and $\Delta F°_{298} = 4640$. (4)

$I_2(g) = 2I(g)$.—The heat capacity of the monatomic gas I is undoubtedly that of other monatomic gases; $Cp = 5\ 0$, that of I_2 is given in Equation 2. Hence

$$\Delta\Gamma = 3\ 5 - 0\ 0040T$$
$$\Delta H = \Delta H_0 + 3.5T - 0.0020T^2$$

The heat of the reaction can be obtained only from the equilibrium measurements of Starck and Bodenstein,[1] from which we have constructed Table I.

<div align="center">TABLE I</div>

T	K	$\Delta F°$	$\Delta H.$	I
1073	0 0114	9550		—2 04
			35670	
1173	0 0474	7115		—1 94
			37000	
1273	0 165	4560		—1 94
			37840	
1373	0 492	1940		— 01
			39640	
1473	1 23	—614		—2 02
			Mean, 36860	— 1 99

The first column gives the absolute temperature, the second the equilibrium constant,[2] the third gives the corresponding free energies, the fourth gives the values of ΔH calculated from consecutive pairs of K, and the fifth the values of I, which are ultimately obtained from the several values of K. The mean value of ΔH at the average temperature of 1273° A leads to $\Delta H_0 = 35650$ cal. Hence,

$I_2(g) = 2I(g);\ \Delta F° = 35650 - 3.50T\ln T + 0\ 0020T^2 - 1\ 99T$ (5)

This equation agrees at least as well with the experimental data of Bodenstein and Starck as the equation which they use. From our equation we find

$$\Delta F°_{298} = 29290 \text{ cal.}$$ (6)

$I(s) = I(g)$.—Combining (4) and (6); (3) and (5), $\Delta F°_{298} = 16965$,

$$\Delta F° = 26275 + 1.60T\ln T - 40.36T.$$ (7)

$2I(s) = I_2(aq.)$.—The free energy of formation of a molal solution of iodine in water can readily be determined from solubility measure-

[1] Starck and Bodenstein, Z. Electrochem., 16, 961 (1910)

[2] The equilibrium constant here given is, as usual, the one involving gaseous pressures (sometimes designated as Kp). It has been calculated from the values of Kc given by Bodenstein.

ments.   Jakowkin[1] found the solubility of iodine at $25°$ to be 0 001334M. This value is corroborated by the work of Hartley and Campbell.[2]   Bray and MacKay[3] show that some of the iodine dissolved is not present as such owing to hydrolysis, and they give the true solubility as 0 00132M.

Assuming now that the activity of I_2 in solution is proportional to its concentration, the free energy of a molal solution is given by the equation

$$\Delta F°_{298} = -R'T \ln 0\ 00132 = 3926 \text{ cal.} \tag{8}$$

Hydrogen Iodide.

$^1/_2H_2 + {}^1/_2I_2(g) = HI(g)$.—This reaction was carefully studied by Bodenstein,[4] and the work has been subjected to a careful critique by Haber in his "Thermodynamics of Technical Gas Reactions."   Haber expresses Bodenstein's data by the free energy equation

$$\Delta F° = -89.575 - 1.575T \ln T + 0.00549T^2 + R'T \ln \frac{p_{HI}}{(p_{I_2}\ p_{H_2})^{1/2}} + 2.67T.$$

From this equation $\Delta H_{298} = -96$ cal. and $\Delta F°_{298} = -1480$ cal.

This equation, as we shall see, gives values of $\Delta F°$, ΔH, and $\Delta \Gamma$, which are by no means consistent with those obtained in other ways   Haber suggested the possibility that the dissociation of iodine into monatomic vapor might have caused some error in the calculations based upon Bodenstein's measurements. Since then, the investigation of Bodenstein and Starck has permitted us to calculate the actual dissociation of I_2 at the various temperatures and pressures used by Bodenstein.   Thus, from Equation 5 of this paper we have calculated the fraction of I_2 dissociated at the four absolute temperatures given in Table II.

TABLE II

T	553	633	713	793
Fraction I_2 dissociated				
(p_{I_2} = 1)	1 50 × 10^{-5}	1 35 × 10^{-4}	0 65 × 10^{-3}	2 45 × 10^{-2}
Fraction I_2 dissociated				
(p_{I_2} = $^1/_4$)	3 01 × 10^{-5}	2 51 × 10^{-4}	1 31 × 10^{-3}	4 90 × 10^{-2}

From this table we may make the small corrections to Bodenstein's equilibrium constants at the four temperatures which we have chosen as representative.   In Table III the value of $\ln K$, which Haber gives, are shown in the second column, the values of $\ln K$ corrected for the dissociation of the iodine in the third, and in the fourth the values of $\Delta F°$ obtained from $\ln K$ (cor.).

[1] Jakowkin, Z phys Chem , **18**, 590 (1895)

[2] Hartley and Campbell, J Chem Soc , **93**, 741 (1908)

[3] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910), **33**, 1485 (1911)

[4] Bodenstein, Z physik Chem , **29**, 295 (1899), and earlier papers

TABLE III

T	ln K (Haber)	ln K (cor)	ΔF°.	I.
553	2 2229	2 2229	—2440	—2 40
633	2 0983	2 0984	—2640	—2 52
713	1 9631	1 9638	– 2780	—2 51
793	1 8195	1 8219	—2870	—2 50

From these data it is theoretically possible to repeat Haber's procedure and obtain a free energy equation with four constants, representing the values of ΔH_0, $\Delta\Gamma_0$, $\Delta\Gamma_1$, and I, and we thus find for ΔH_0, 465 2, instead of Haber's – 89 6, for $\Delta\Gamma_0$, —0 246 instead of 1.575, and for $\Delta\Gamma_1$ —0.008 instead of —0 011. Now this work of Bodenstein is perhaps the most careful investigation of a gaseous equilibrium that is to be found in the literature, and the calculation that we have just made shows how impossible it is to use any such body of data, obtained over a small temperature range, for the calculation of such quantities as $\Delta\Gamma_0$ and $\Delta\Gamma_1$, since the corrections which we made amounted to hardly more than the probable experimental error and yet have produced enormous changes in the calculated thermal quantities.

We must, therefore, proceed in this case as in others and obtain our chief knowledge of the thermal data from calorimetric measurements. We have previously obtained

$$Cp(HI) = 6\ 5 + 0\ 0010T$$
$$Cp(^1{}_2H_2) = 3\ 25 + 0\ 00045T$$
$$Cp(^1{}_2I_2) = 3\ 25 + 0\ 0020T$$

Hence,

$$\Delta\Gamma = 0\ 00 - 0\ 00145T \tag{9}$$

Thomsen gives 6000 and Berthelot 6300 cal. (average 6150) as the value of ΔH for the formation of HI from solid iodine at room temperature We have already seen that the heat of sublimation of iodine at room temperature is 7550 cal. Hence for our reaction $\Delta H_{291} = -1400$ and from (9) $\Delta H_0 = -1340$ cal. Thus,

$$^1/_2H_2 + {}^1/_2I_2(g) = HI(g),\ \Delta F° = -1340 + 0\ 000725T^2 - 2\ 48T \tag{10}$$

where the value of I is the average obtained from the four values of ΔF given in Table III.

Hence we find $\Delta F°_{298} = -2010$ cal.

The value of $\Delta F°_{298}$ thus calculated is corroborated by the work of Stegmuller,[1] who measured the electromotive force of a cell with hydrogen and iodine electrodes and hydrogen iodide solution as electrolyte. The pressures of H_2, I_2 and HI were all measured. His results are given in Table IV, where the first column shows the centigrade temperature, the second the values of $\Delta F°$ obtained from the e. m. f., the third the

[1] Stegmuller, Z Electrochem., 16, 85 (1910)

values of ΔF° calculated from Equation 10, and the fourth the values of I obtained from Stegmuller's results

TABLE IV

t	ΔF°	ΔF° calc	I
31 6	—2036	—2028	—2 5
55 2	—2019	—2073	—2 3
81 6	—1958	—2130	—2 0

It is evident that some error, perhaps due to the neglect of the liquid potential between the HI solution and the HI solution saturated with I_2, has given a false temperature trend to Stegmuller's results, but his value at the lowest temperature is in almost perfect agreement with Equation 10

$\frac{1}{2}H_2(g) + I(s) = HI(g)$ —By combining Equations 3 and 10 we find for this reaction $\Delta F^\circ_{298} = 310$ cal and

$$\Delta F^\circ = 7110 + 3\ 35T \ln T - 0\ 000275T^2 - 41\ 845T \quad (11)$$

Iodide Ion.

$\frac{1}{2}I_2(aq) + \ominus = I^-$ —The most accurate investigation of this electrode potential to be found in the literature is that of Maitland,[1] who obtained for the cell $I_2(aq),I \parallel N\ E$, $E^\circ_{298} = -0\ 3415v$, E° being calculated from the measured value of E by the equation[2]

$$E = E^\circ + \frac{RT}{F} \ln \frac{(I^-)}{(I_2)^{1/2}}$$

Some unpublished measurements made by Dr P V Farragher in this laboratory fully corroborate Maitland s experimental work   But the recent investigations of Lewis upon the ratio of activity to concentration show that Maitland s result is subject to a small correction   Instead of attempting to calculate the magnitude of this correction, Farragher has studied the same cell at lower concentrations and has found that with increasing dilution of I_2 and of I^- the normal e m f reaches the constant value $E^\circ_{298} = -0\ 3407$

We have found in the preceding paper[3] $N\ E \parallel H^+, H_2, E^\circ_{298} = -0\ 2776$ Hence for the cell $I_2(aq),I^- \parallel H^+,H_2$, $E^\circ_{298} = -0\ 6183$ This then is the normal potential of an electrode involving dissolved iodine and iodide ion   From the equation $\Delta F = -nEF'$, n being in this case —1, we find

$$\frac{1}{2}I_2(aq) + \ominus = I^-, \Delta F^\circ_{298} = -14267 \quad (12)$$

$I(s) + \ominus = I^-$ —Combining Equations 8 and 12

$$\Delta F^\circ_{298} = -12304 \quad (13)$$

[1] Maitland Z' Electrochem 12, 263 (1906)
[2] The conventions employed in such electromotive force equations are stated by Lewis (THIS JOURNAL 35, 22 (1913)) see also footnote to the page cited
[3] Lewis and Randall THIS JOURNAL 36, 1975 (1914) Equation 18

Tri-Iodide Ion.

$I^- + 2I(s) = I_3^-$.—The equilibrium between iodide and tri-iodide is one in which some unusually large apparent deviations from the law of the perfect solution are evident, even at high dilutions, as shown by Bray and MacKay.[1] In the presence of solid iodine the ratio of potassium iodide to potassium tri-iodide should be constant, provided that the degree of dissociation of the two salts is the same function of the concentration. As a matter of fact, however, the ratio is not constant even in fairly dilute solutions, as shown by Table V (Bray and MacKay), in which the first row shows the total concentration of potassium salt, and the second the ratio of potassium iodide to potassium tri-iodide in solutions in which the activity of the iodine was kept constant by the presence of an excess of solid iodine. The measurements were at $25°$.

TABLE V

ΣK	0 100	0 020	0 010	0 005	0 002	0 001	0 0
KI/KI_3	0 99	1 04	1 06	1 08	1 11	1 14	1 16

Bray and MacKay assume that the degree of dissociation of these two salts is the same, and that the activity of the tri-iodide ion is abnormal. Making the same assumption here and using the value at infinite dilution, we find for our reaction,

$$\Delta F°_{298} = -R'T \ln (1/1 . 16) = 88 \text{ cal.} \qquad (14)$$

When working, however, with any appreciable concentration of I_3^- we must, for the present, make use of the empirical tables of Bray and MacKay, and of Jakowkin.[2]

$3I(s) + \ominus = I_3^-$.—Combining (13) and (14) gives

$$\Delta F°_{298} = -12216. \qquad (15)$$

Hypoiodous Acid.

$I_2(aq.) + H_2O(l) = H^+ + I^- + HIO(aq.)$.— The hydrolysis of iodine leads to the reversible formation of hydriodic and hypoiodous acids, the latter of which, a very weak acid, is present in the un-ionized state. The degree of hydrolysis has been investigated by Bray[3] and by Bray and Connolly[4] through measurements of the conductivity of solutions of iodine in water. They find at $25°$ for the equilibrium constant,[5]

$$K = (H^+)(I^-)(HIO)/(I_2) = 3 \times 10^{-13}.$$

Hence,

$$\Delta F°_{298} = -R'T \ln (3 \times 10^{-13}) = 17100 \qquad (16)$$

[1] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910)

[2] Jakowkin, Z physik Chem , **20**, 19 (1896).

[3] Bray, THIS JOURNAL, **32**, 932 (1911)

[4] Bray and Connolly, Ibid , **33**, 1485 (1911).

[5] Skrabal, Z. Elektrochem , **17**, 665 (1911), by a more indirect method obtained a value between 3 and 4 times as great as this.

$I(s) + \frac{1}{2}O_2 + \frac{1}{2}H_2 = HIO(aq.)$.—Combining Equations 8, 13 and 16 of this paper with 8 and 53 of the preceding paper, on oxygen and hydrogen compounds, gives

$$\Delta F^{\circ}_{298} = -23300 \qquad (17)$$

The degree of dissociation of HIO as an acid is extraordinarily small, and has not been quantitatively determined. It is therefore impossible to calculate the free energy of the hypoiodite ion.

Iodate Ion.

In order to determine the free energy of formation of the iodate ion we may consider the following subsidiary reactions:

$3I_2(aq.) + 3H_2O + 5AgIO_3(s) = 5AgI(s) + 6H^+ + 6IO_3^-$.—This re-action is one which was studied by Sammet,[1] who investigated the equilibrium at 25° in a system comprising a solution of HIO_3 and I_2, and solid AgI and $AgIO_3$, the concentration of the I_2 being determined by shaking out with carbon tetrachloride, that of HIO_3 by analysis. The equilibrium constant is

$$K = \frac{(H^+)^6(IO_3^-)^6}{(I_2)^3}.$$

It is in just such a reaction as this where ions enter only on one side of the reaction that we might expect a great variability of K with the concentration, if the ion concentrations are calculated from the conductivities by Kohlrausch's rule. By a curious chance, however, Sammet, using old and unquestionably incorrect conductivity values, obtained degrees of dissociation identical with our calculated corrected degrees of dissociation of substances of the type of HIO_3. Consequently, K was found to be a constant, and its average value, in the five cases in which the concentration of acid did not exceed $0.1M$, was 0.000853. Hence,

$$\Delta F^{\circ}_{298} = 4190 \qquad (18)$$

$AgIO_3 = Ag^+ + IO_3^-$.—We may employ the solubility product of $AgIO_3$, which, at 25°, is found to be 3.5×10^{-8} by Noyes and Kohr;[2] 3.1×10^{-8} by Hill and Simons;[3] and about 3.2×10^{-8} by Kohlrausch.[4] The value of 4.5×10^{-8} obtained by Sammet is doubtless quite erroneous. We may take as the average of the first three, 3.3×10^{-8}, whence

$$\Delta F^{\circ}_{298} = 10220 \qquad (19)$$

$AgI + \frac{1}{2}H_2 = Ag + H^+ + I^-$.—On account of the extreme dis-cordance of the values given in the literature for the solubility of silver iodide we shall, instead of making use of the free energy of solution of

[1] Sammet, *Z. physik. Chem.*, **53**, 641 (1905).

[2] Noyes and Kohr, *Ibid.*, **42**, 338 (1903).

[3] Hill and Simons, *Ibid.*, **67**, 602 (1909).

[4] Kohlrausch, *Ibid.*, **64**, 151 (1908).

AgI, employ the results of Danneel,[1] who studied the reversible reaction between hydrogen and silver iodide The temperature of his measurements was variable, ranging from 13° to 17° Fortunately the equilibrium constant of this reaction changes little with the temperature, and we may conclude from his measurements that at 25° Ag and AgI are in equilibrium with hydrogen at 1 atms and HI at 0 05M Taking the corrected degree of dissociation at this concentration as 0 82, the concentration of H^+ and of I^- is 0 041M and

$$\Delta F^°_{298} - - 2R''T \ln 0\ 041 = 3800^2 \qquad (20)$$

We have found in Equations 13 and 8 the free energy of iodide ion, and of aqueous iodine, and in the preceding paper on oxygen and hydrogen compounds the free energy of water, of silver ion, and of hydrogen ion, Equations 53, 50, and 8 We may combine all these equations as follows

$5AgIO_3 + 3I_2(aq) + 3H_2O(l) = 5AgI + 6H^+ + 6IO_3^-$	$\Delta F^°_{298} = 4190$
$5Ag^+ + 5IO_3^- = 5AgIO_3,$	$\Delta F^°_{298} = -51100$
$5AgI + 5/2H_2 = 5Ag + 5H^+ + 5I^-$	$\Delta F^°_{298} = 19000$
$5I^- + 5 \oplus = 5I(s),$	$\Delta F^°_{298} - 61520$
$6I(s) = 3I_2(aq),$	$\Delta F^°_{298} = 11780$
$3H_2 + 3/2O_2 = 3H_2O(l),$	$\Delta F^°_{298} = -169860$
$11H^+ = 11/2H_2 + 11 \oplus$	$\Delta F^°_{298} = 0$
$5Ag + 5 \oplus = 5Ag^+,$	$\Delta F^°_{298} = 92120$
$I(s) + 3/2O_2 + \ominus = IO_3^-,$	$\Delta F^°_{298} = -32350$
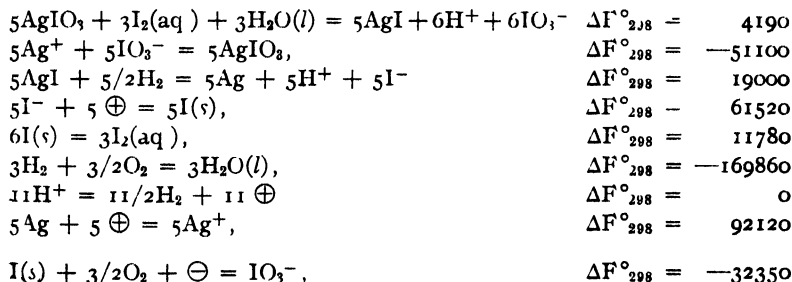
The eight equations are added as they stand to give the equation for the free energy of the iodate ion We shall not, however, number this equation as there is another, presumably more accurate, method of determining this free energy which we shall consider presently It is difficult to estimate the accuracy of the calculation which we have just made Each of the individual measurements seems fairly reliable, but there is large opportunity for the multiplication and accumulation of errors in the whole calculation

$I(s) + 3H_2O(l) + 5 \oplus = 6H^+ + IO_3^-$ —A more accurate method of determining the free energy of the iodate ion is furnished by the e m f. measurements of Sammet, who determined the potential corresponding to the above reaction A platinum electrode in contact with 0 001M HIO_3 and solid iodine, against the normal calomel electrode at 25° gave

[1] Danneel Z physik Chem 33, 439 (1900)

[2] By combining this value with the free energy of formation of H^+ of I^- and of Ag^+ we find for the free energy of formation of AgI, $F^°_{298} = -16100$ and for the solubility of AgI at 25°, 7 2 × $10^{-9}M$ This is only about 70% of the solubility obtained by Goodwin and by Thiel from e m f measurements A far more accurate value could be readily obtained by a repetition of Danneel's work at 25°

$E = -0\ 665$, exclusive of liquid potentials. The potential of the normal calomel electrode we have found in the preceding paper to be -0.2776. The absolute potential, therefore, of the above electrode is $-0\ 943$. Hence we may obtain the normal potential of this electrode from the equation $-0.943 = E°_{298} - (0.05915/5)\log(H^+)^6(IO_8^-)$. Assuming the degree of dissociation of $0.001M$ HIO_3 to be $0\ 97$, the concentration of each ion is $0.00097M;$

$$E°_{298} = -1.193; \quad \Delta F°_{298} = -5EF' = 137590. \quad (21)$$

$I(s) + 3/2O_2 + \ominus = IO_3^-$.—Combining Equation 21 with the value we have used above for the free energy of formation of liquid water and of hydrogen ion, we find

$$\Delta F°_{298} = -32270 \quad (22)$$

This value is in surprisingly good agreement with the one obtained above. The latter calculation is by far the more reliable of the two and can hardly be in error by more than 200 calories.

In concluding we wish to express our obligation to the Rumford Fund of the American Academy of Arts and Science for financial aid in this investigation.

Summary.

We shall not summarize here the various subsidiary calculations used in this paper, but merely repeat the final values of the free energy of formation of the iodine compounds investigated.

TABLE VI

Substance	$\Delta F°_{298}$	Equation	Substance	$\Delta F°_{298}$	Equation.
$I(s)$	0		$HI(g)$	310	11
$I(l)$	460	1	I^-	—12304	13
$I_2(g)$	4640	4	I_3^-	—12216	15
$I(g)$	16965	7	$HIO(aq)$	—23300	17
$I_2(aq)$	3926	8	IO_3^-	—32270	22

BERKELEY, CALIFORNIA.

A SENSITIVE CRITERION OF THE PRECISION AND OF CONSTANT ERRORS IN THE CONDUCTANCE DATA OF WEAK ELECTROLYTES, THE DETERMINATION OF THE MOLAR CONDUCTANCE OF ORGANIC ELECTROLYTES AT ZERO CONCENTRATION AND A STUDY OF THE CORRECTION FOR THE SPECIFIC CONDUCTANCE OF THE CONDUCTIVITY OF WATER.

BY C. G. DERICK.

I. "Calculated" λ_0 as a Criterion of Precision.

If the ideal mass law for weak electrolytes is given the form $k = (\alpha^2/_1 - \alpha)$ or $k = c\lambda/\lambda_0(\lambda_0 - \lambda)$, since $\alpha = \lambda/\lambda_0$, is assumed to hold

exactly in any given case, it is possible to calculate the value of the conductance at zero concentration or infinite dilution from two measurements of its conductance at two different concentrations. If λ and λ_1 represent the molar conductances of this electrolyte at the concentrations C and C_1, respectively, then $k = c\lambda^2/\lambda_o(\lambda_o - \lambda) = c_1\lambda_1^2/\lambda_o(\lambda_o - \lambda_1)$ from which $\lambda_o = \lambda\lambda_1(c\lambda - c_1\lambda_1)/(c\lambda^2 - c_1\lambda_1^2)$.[1]

Since the ideal mass law in the above form can only hold rigorously where the nature of the solution no longer changes with change in concentration, it is obvious that the mass law in this form is never rigorously obeyed.

Yet there may exist electrolytes which obey it accurately enough so that our measurements do not detect any deviations at small concentrations. Fortunately, data are fast being accumulated which show to what degree the ideal mass law in the above form is approximated and may be used, therefore, to draw valuable conclusions concerning the behavior of electrolytes, as, for example, the calculation of the molar conductance at zero concentrations in the manner just described. The recent accurate work of Kendall[2] upon the conductance of acetic acid in aqueous solution at 25° warrants one in believing that this acid very close' · approximates the ideal mass law in the above form, and it may be used in the calculation of the molar conductance of acetic acid at zero concentration, which value will hereafter be called the "calculated" λ_o. Table I, that follows, gives the results of these calculations for all possible combinations of the dilutions measured by Kendall together with the corresponding values for its molar conductance and ionization constant.

As stated in the introductory paragraphs to the article, in order to calculate λ_o, as has been done in the table, the mass law in the above form is assumed to be approximated to such a degree that experimental errors in the measured values of λ and λ_1, and C and C_1 are not greater than those introduced by the difference in · alues for the ionization constant corresponding to these concentrations, since these values are made identical in the calculations. The values given by Kendall for the ionization constant corresponding to the different concentrations or dilutions, as seen from the table, justify the above assumptions and it is evident that small differences in these values do not influence the "calculated" λ_o appreciably. The concentrations, at which the constant for ideal mass law in the above form is most accurately known, may be determined as follows: The percentage error introduced into the ionization constant by errors in λ and λ_o (C is assumed to have a negligible error, $i.\ e.$, is a

[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," **1898**, p 103

[2] *J Chem Soc*, **101**, 1283 (1912); and *Meddelanden fran K. Vetenskapsakademiens Nobelinstitut*, **2**, 38 (1913)

TABLE I
Conductance data [1]

v	λ	$k_a^{m\,o} \times 10^{-5}$
13 57	6 086	1 845
27 14	8 591	1 851
54 28	12 09	1 849
108 56	16 98	1 849
217 1	23 18	1 851
434 2	33 22	1 849
868 4	46 13	1 850
1737 0	63 60	1 854
3474 0	87 17	1 855
6948 0	116 8	1 870
∞	387 7	

"Calculated" λ₀		"Calculated" λ₀		Calculated λ₀	
Dilutions	λ₀	Dilutions	λ₀	Dilutions	λ₀
12 57 and 27 14	766	54 28 and 108 56	290*	217 1 and 434 2	379*
54 28	449	217 1	402	868 4	388
108 56	359	434 2	391	1737 0	393
217 1	416	868 4	392	3474 0	392
434 2	402	1737 0	395	6948 0	398
868 4	399	3474 0	393	434 2 and 868 4	394
1737 0	399	6948 0	399	1737 0	398
3474 0	396	108 56 and 217 1	551*	3474 0	394
6948 0	400	434 2	434*	6948 0	400
27 14 and 54 28	348	868 4	414*	868 4 and 1737 0	400*
108 56	311	1737 0	408*	3474 0	381
217 1	389	3474 0	401*	6948 0	401
434 2	384	6948 0	403*	1737 0 and 3474 0	390
868 4	388			6948 0	401
1737 0	532			3474 0 and 6948 0	409
3474 0	391				
6948 0	458				

constant for the given case) is easily obtained by differentiating the logarithmic form of expression $k = C\lambda^2/\lambda_o(\lambda_o - \lambda)$, whence

$$dk/k = [(2\lambda_o - \lambda)/(\lambda_o - \lambda)][d\lambda/\lambda - d\lambda_o/\lambda_o].$$

As the solutions become more concentrated, λ approaches zero as its limit when $dk/k = 2[d\lambda/\lambda - d\lambda_o/\lambda_o]$. On the other hand, as the solution becomes more dilute, λ approaches λ_o as its limit, when $dk/k = \infty (d\lambda/\lambda - d\lambda_o/\lambda_o)$ Obviously, the ionization constant is least influenced by errors in λ and λ_o the greater the concentration, which, however, must never be so great that the degree of ionization ceases to be measured by the expression $\alpha = \lambda/\lambda_o$ with the requisite accuracy for the above discussion. For most weak electrolytes, the value of this upper limit of concentration is in the neighborhood of 0.02 N according to recent investigations. Thus, for Kendall's measurements the value 1.849×10^{-5}

[1] Uncorrected for the specific conductance of the conductivity water.

may be taken as the ionization constant of acetic acid according to his data. The error in this value may be greater or less than that in λ or λ_o accordingly as $d\lambda/\lambda$ and $d\lambda_o/\lambda_o$ are of the opposite or the same sign, respectively. Before the correct weight can be given to this value for the ionization constant for acetic acid the amount and the direction of the errors in λ and λ_o must be ascertained. However, it is sufficiently obvious that acetic acid very closely approximates the mass law and that a correct value for its "calculated" λ_o may be found as described.

It is now necessary to determine which value of "calculated" λ_o is most free from the errors in λ and λ_1 or which value is most sensitive to these errors if the "calculated" λ_o is to be used as a criterion of the accuracy of the conductance data. In a similar manner to that in which the percentage error in the ionization constant was found, and again assuming that the errors in C and C_1 are negligible, the percentage error in λ_o with those in λ and λ_1 may be calculated from the expression:

$$\frac{d\lambda_o}{\lambda_o} = \frac{C_1\lambda_1[C_1\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1]d\lambda}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]} \frac{d\lambda}{\lambda} + \frac{C\lambda[C_1\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]} \frac{d\lambda_1}{\lambda_1}$$

Letting $a = \dfrac{C_1\lambda_1[C_1\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}$, $b = \dfrac{C\lambda[C_1\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}$

and solving for their numerical values in the following cases, using the data given in Table I, the results of Table II are obtained:

TABLE II

C	C_1	k_c	k_{c_1}	a	b.
1/54 28	1/108 56	1 849 $\times$ 10^{-5}	1 849 $\times$ 10^{-5}	—110 5	+111 2
1/54 28	1/434 2	1 849 $\times$ 10^{-5}	1 849 $\times$ 10^{-5}	— 33 4	+ 34 4
1/54 28	1/6948	1 849 $\times$ 10^{-5}	1 870 $\times$ 10^{-5}	— 5 3	+ 6 3
1/108 56	1/217 1	1 849 $\times$ 10^{-5}	1 851 $\times$ 10^{-5}?	—151 1?	+151 9?
1/217 1	1/434 2	1 851 $\times$ 10^{-5}	1 849 $\times$ 10^{-5}	— 71 5	+ 72 5
1/434 2	1/868 4	1 849 $\times$ 10^{-5}	1 850 $\times$ 10^{-5}	— 51 6	+ 52 7
1/868 4	1/1737 0	1 850 $\times$ 10^{-5}	1 854 $\times$ 10^{-5}	— 36 0	+ 37 3

From Table II it is seen that the error in "calculated" λ_o for acetic acid is never greater than that in λ or λ_1, depending upon which is most in error, as long as $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ have the same sign, since (a) and (b) always have opposite signs. This appears to be the case with Kendall's data. As long as this is true the "calculated" λ_o may be found with the same accuracy whatever combinations of λ and λ_1 (C and C_1) are employed, provided the ideal mass law in the above form is approximated with sufficient accuracy. In other words, the "calculated" λ_o is an equally sensitive criterion of the precision of the molar conductances under these conditions whatever the values of C and C_1.

If, however, $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$, are opposite in sign, then the error in "calculated" λ_o is greater the greater the value of C and C_1, since (a) and

(*b*) always have opposite signs. Table II shows that for Kendall's data on acetic acid, that the "calculated" λ_o, found by using concentration which are as different as possible, is least affected by errors in λ and λ_1 when $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ are opposite in sign. Thus in the series of values of "calculated" λ_o in which $C = 1/54.32$ (Table I) is the common concentration, when $C_1 = 1/6948$, the "calculated" λ_o is 399; while the average of all the values of "calculated" λ_o for all possible combinations of concentrations from $1/54.32$ to that of $1/6958$, excluding those marked by the asterisks, is 398 with a mean error of ± 6 for each value. It is also clear that "calculated" λ_o is a much more sensitive criterion of the precision of the conductance data when C and C_1 are as near in value as possible if $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ are opposite in sign.

II. "Calculated" λ_o as a Criterion of Constant Errors.

The mathematical methods for the determination of the precision of experimental results have been very accurately developed and employed for conductance data, but such methods are of little value where constant errors are present. It is the presence of constant errors in most of the conductance data of weak electrolytes that renders the same useless when quantitative conclusions are to be drawn. Therefore, more attention must be paid to the development of methods for the detection of such constant errors in conductance data.

In the present discussion, fortunately, the molar conductance at zero concentration for weak electrolytes, like acetic acid, which closely approximate the ideal mass law in the above form, may be determined, independently of the conductance data for the acid, by the following well-known method:

$$\lambda_o RCO_2H = \lambda_o RCO_2Na + \lambda_o H^+ - \lambda_o Na^+$$

The mobilities of the hydrogen and sodium ions are known from conductance and transference measurements upon strong acids and their salts. The molar conductances of the sodium or other salts of the weak acid are extrapolated to zero concentration by one of the well-known methods in order to determine their molar conductance at zero concentration. In this manner, by independent measurements, the molar conductance at zero concentration of a weak electrolyte may be determined. Such a value for λ_o will be spoken of as determined by the salt method in the following discussion:

A comparison of the "calculated" λ_o for weak electrolytes like acetic acid with that obtained for the same acid by the salt method offers a means of detecting constant errors in conductance data. This means assumes that the conductance data for the salt is fairly accurately known and, similarly for the values of the mobilities of the sodium and hydrogen ions. It is not necessary that the weak electrolyte approximate the ideal

mass law, in the above form, as accurately as does acetic acid in order that "calculated" λ_0 may be used to detect constant errors in conductance data, as will be shown from the discussions in the following sections. It must be pointed out, however, that the conductance at zero concentration for most uni-univalent salts of weak electrolytes falls between the limits 80 and 90 while the mobility of the hydrogen ion at 25° for aqueous solution has been given the limits 338 and 365.[1] Obviously, fairly large errors in the molar conductance at zero concentration for the sodium salt will not introduce a correspondingly large error in the λ_0 value determined by the salt method, since the former value is additive in the above equation to the mobility of hydrogen and sodium ions. Similarly it is not necessary that the mobility of the sodium ion be known with anything like the accuracy with which the mobility of the hydrogen ion must be known, since the value of the former is 52 compared 338 to 365 for the latter at 25°. Unfortunately, the uncertainty is greatest concerning the mobility of the hydrogen ion, which should be most accurately known.

Kendall, in the article referred to above, has recently attempted to ascertain the most accurate value for the mobility of the hydrogen ion at 25°. His indirect method consisted in the calculation of the ideal mass law constant from his measurements of the conductance of cyanoacetic, o-nitrobenzoic, o-chlorobenzoic, etc., acids at concentrations where these acids very closely approximated this law. These calculations were made with varying values for the mobility of the hydrogen ion, provided it was always in the neighborhood of 350 and that value was chosen for this mobility which gave the most consistant mass law constant at the smaller concentrations. His method gave him the value 347.2, provided the specific conductance of water was not greater than 0.9×10^{-6}. No correction was made for such water.

Table V, with the subsequent discussion, offers convincing proof of the correctness of this value for the mobility of the hydrogen ion at 25° for transition electrolytes in aqueous solution. For, in Kendall's work, he must assume the mass law and draw his conclusion from the mass law constant, which is in reality reasoning in a circle; since he had no independent measurements to justify his assumption of the mass law for his measurements. The calculation of the "calculated" λ_0 from the conductance data of these acids, as has been done in Table V, while also assuming the mass law, gives a value which may be checked by independent measurements and thus justify the assumption of the mass law. This procedure entirely substantiates the conclusions drawn by Kendall as to the mobility of the hydrogen ion at 25° for transition electrolytes, which is apparently, as the theories demand, the same value as for strong electrolytes.

[1] See article by Kendall mentioned above.

In the case of weak electrolytes ($k < 10^{-4}$) Kendall justly states that his method for determining the mobility of the hydrogen ion is not sensitive, since large variations in this value do not influence the ionization constant to anything like the extent that it does for the transition electrolytes. In fact the water correction, which has a slight influence for the transition electrolytes, is of much more importance than slight variation in the value for the mobility of hydrogen ions upon the ionization constants of weak electrolytes, as will be discussed later. However, in accordance with theory, Kendall uses the value 347 for the mobility of the hydrogen ion in acetic acid at 25°, and calculates what he considers the best ionization constant for acetic acid at 25°, as was seen in Table I. In this case the unsatisfactoriness of his method, when applied to weak electrolytes for the solution of this problem, becomes very evident, since he did not choose the best value for the conductance of acetic acid at zero concentration, *i. e.*, the best value for the mobility of the hydrogen ion, which gives the best mass law constant for his data. In determining the molar conductance at zero concentration for acetic acid, Kendall used the value for the mobility of the acetate ions at 25° which was determined many years ago by Ostwald[1] and compiled by Bredig,[2] which, when expressed in reciprocal ohms, is 40.7. Since the limits for the mobility of the hydrogen ion at 25° are 338 and 365, the limits for the molar conductance at zero concentration of acetic acid at 25° are 379 and 406, accepting the mobility of the acetate ion as 41. Obviously, that value, for λ_0 for acetic acid, which will give the best mass law constant is found by assuming the mass law to hold, and solving for λ_0 from the conductance data of the acid as was done in Section I. This value for "calculated" λ_0 was found to be 398, which value is well within the above limits. Table III gives the values for the ionization constant of acetic acid determined by using this "calculated" λ_0 value, together with those of Kendall, using his data for λ and λ_0.

TABLE III.

| | Ionization constant × 10^{-5}. | | | Ionization constant × 10^{-5}. | |
Dilutions	Kendall.	Author	Dilutions.	Kendall.	Author.
13 57	1 845	1 749	434 2	1 849	1.750
27 14	1 851	1 752	868 4	1 850	1 750
54 28	1 849	1 752	1737 0	1 854	1 750
108 56	1 849	1 749	3474 0	1 855	1 749
217.1	1 851	1 750	6948 0	1 870	1 755

Kendall's measurements and interpretation give the average value for the ionization constant of acetic acid at 25° as 1.852×10^{-5} with a mean error in each value of $\pm 7 \times 10^{-8}$, while the author's interpretation gives the average value $1\ 750 \times 10^{-5}$ with the mean error in each

[1] *Z. physik. Chem.*, **2**, 45 (1889).
[2] *Ibid.*, **13**, 218 (1894)

value of $\pm 2 \times 10^{-5}$. In the term $(\lambda_0 - \lambda)$ employed in these calculations, λ was rounded off to a whole number, except where the decimal was close to 0.5 of a unit, so that the above results for the ionization constant are as uniform as possible, since the value for λ_0 is not known to a fraction of a whole unit. This value is practically the same as that obtained by Ostwald[1] when his results are expressed in international units, using the accepted values for the mobilities of the sodium and hydrogen ions at $25°$ (51.2 and 347). Kendall stated that Ostwald obtained the value 1.80×10^{-5} for this constant, but overlooked the fact that the values for these mobilities had changed since Ostwald made his calculations.

The fact that Kendall's data for acetic acid give the value 398 for the "calculated" λ_0 while the salt method gives 388 means that some constant error is present in these data, if the mobility of the hydrogen ion at $25°$ is 347 for such weak electrolytes. This constant error may be due to the fact that no correction was made for the specific conductance of the water used in the dilutions (see last section).

Finally, it is interesting to note that this value for "calculated" λ_0 for acetic acid is much closer to that obtained by the salt method by using the mobility of the hydrogen ion as 365 as suggested by Noyes and Sammuel.[2]

III. Application of the Criterion, "Calculated" λ_0 to other Data upon the Conductance of Acetic Acid.

In order to test the precision of, and constant errors in, the conductance data for acetic acid that follow, the "calculated" λ_0 was determined for all possible combinations of concentrations as given in Table IV.

TABLE IV.
Conductance Data.

Ostwald[3] 25°.			Jones[4] 25°.			Van't Hoff[5] 19.1°.	
v.	λ.	$k_a^{25} \times 10^{-5}$.	v.	λ.	$k_a^{25} \times 10^{-5}$.	v.	λ.
8	4.61	1.75	2	2 089	1 69	18.53	7.110
16	6.48	1.74	8	4.342	1.83	37.07	9 970
32	9.19	1.68	32	8.699	1.86	74.15	14.03
64	12.81	1 73	128	17.11	1.84	148.3	19.76
128	18.03	1.74	512	33.24	1.82	296.6	27 53
256	25.23	1.74	1024	45 87	1.81	593 2	38.16
512	34.73	1 63	2048	63.00	1.80	1186.4	49 60
1024	48.90	1.74				2372.8	71.65
						4745.6	97.36
						9491.2	129.7

[1] *Z. physik. Chem.*, **3**, 170 (1889).
[2] *Ibid.*, **43**, 49 (1903).
[3] *Ibid.*, **3**, 174 (1889).
[4] H. C. Jones, "Electrical Conductivity, etc., of Certain Salts and Organic Acids."
[5] *Z. physik. Chem.*, **2**, 779 (1889).

Table IV (continued)
Calculated λ₀

Ostwald Solutions	λ₀	Jones Solutions	λ₀	Van't Hoff Solutions	λ₀
8 and 16	151	2 and 8 —	28 2	18 54 and 37 07	117
32	645	32 —	82 2	74 17	237
64	234	128 —	348 0	148 3	382
128	1647	512 +	1900	296 6	331
256	358	1024	698	593 2	318
512	216	2048	524	1186 4	312
1024	366	8 and 32 —	1279	2372 8	319
16 and 32	—468	128 +	434	4745 6	344
64	+279	512	345	9491 2	349
128	351	1024	329	37 07 and 74 15	446*
256	412	2048	334	148 3	582*
512	222	32 and 128	434	296 6	384*
1024	388	512	288	593 2	344
32 and 64	135	1024	292	1186 4	328
128	236	2048	308	2372 8	329
256	321	128 and 512	301	4745 6	353
512	185	1024	301	9491 2	363
1024	205	2048	317	74 15 and 148 3	740*
64 and 128	509	512 and 1024	301	296 6	369
236	539	2048	325	593 2	333
512	211	1024 and 2048	344	1186 4	322
1024	414			2372 8	325
128 and 256	562			4745 6	350
512	183			9491 2	361
1024	402			148 3 and 296 6	269*
256 and 512	128			593 2	289*
1024	373			1186 4	298*
512 and 1024	—695			372 8	302*
				4745 6	340*
				9491 2	355*
				296 6 and 593 2	299*
				1186 4	317
				2372 8	315
				4745 6	347
				9491 2	361
				593 2 and 1186 4	336
				2372 8	320
				4745 6	355
				9491 2	359
				1186 4 and 2372 8	281*
				4745 6	334
				9491 2	346
				2372 8 and 4745 6	406*
				9491 2	392*
				4745 6 and 9491 2	384*

The criterion establishes the fact that the measurements by Ostwald and by Jones lack precision and contain constant errors that render them

valueless from a quantitative standpoint when compared to those by Kendall. Further, the criterion establishes the second fact that the errors in λ and λ_1 are often in opposite directions since the value for "calculated" λ_0 may suddenly jump from -468 to $+279$ in the case of Ostwald's measurements, or from -1279 to $+434$ in the case of those by Jones (see Table IV).

The fact that the ionization constants calculated from the measurements of Ostwald, as well as from those by Jones, show a much greater precision than the corresponding values for "calculated" λ_0 must be attributed in part to the fact that there is a compensation in the errors of λ by those of λ_0 since the previous section shows that

$$dk/k = [(2\lambda_0 - \lambda)/(\lambda_0 - \lambda)][d\lambda/\lambda - d\lambda_0/\lambda_0].$$

In other words, the errors in λ and λ_0 must be in the same direction so that $d\lambda/\lambda$ and $d\lambda_0/\lambda_0$ have the same sign. Further, fairly large differences in the values for λ_0 do not greatly influence the value for the mass law constant of acetic acid. These facts make it clear that the use of the criterion, "calculated" λ_0 is much more sensitive as a test for the precision of, and of constant errors in, the conductance data of weak electrolytes than the ionization constant and that its use is indispensible at present, if accurate quantitative conductance data of such electrolytes is desired.

The measurement by van't Hoff and L. Th. Reicher give values for "calculated" λ_0 which fall, as a rule, close to the value determined by the sodium salt method. The average value for "calculated" λ_0 of all the calculations from the dilution 37.07 to that of 9491.2, neglecting those marked by the asterisks, is 345 with a mean error of ± 19 in each value. The most probable value for this quantity by the salt method is not far from 352 at 19.1°.

Finally, the measurements by Kendall (Table I), although they possess satisfactory precision, contain constant errors, provided the mobility of the hydrogen ion at 25° is 347, as maintained by Kendall for acetic acid, since the "calculated" λ_0 is 398 while Kendall chose 388 by the salt method.

IV. Application of the Criterion of "Calculated" λ_0' to the Conductance Data of Transition Electrolytes.

In the case of transition electrolytes, Kendall[1] has pointed out for cyanoacetic, o-chlorobenzoic, o-nitrobenzoic acids, etc., that fairly consistent values for their ionization constants are obtained for solutions sufficiently dilute, provided an arbitrary value was chosen for the mobility of the hydrogen ion (347) and that the specific conductance for the conductivity water was not greater than 0.90×10^{-6}. In general, it is believed that all electrolytes approximate very accurately the mass law in the

[1] See reference above.

TABLE V.

Cyanoacetic acid			o-Chlorobenzoic acid			o-Nitrobenzoic acid		
v	λ	$\lambda_d^{25°} \times 10^{-3}$	v	λ	$\lambda_d^{25°} \times 10^{-3}$	v	λ	$\lambda_d^{25°} \times 10^{-3}$
20 80	96 2	0 398	150 1	134 6	0 1293	32	139 7	6 72
41 60	127 1	0 389	300 2	174 0	0 1286	64	179 0	6.60
83 20	164 5	0 381	600 4	218 0	0 1284	128	221 0	6 45
166 4	207 3	0 375	1201 0	262 6	0 1284	256	265 0	6 33
332 8	252 4	0 372	2402 0	302 1	0 1279	512	303 6	6 28
665 6	294 4	0 372	4804 0	333 0	0 1286	1024	333 5	6 27
1331 0	329 2	0 372	9608 0	353 7	0 1288	2048	353 6	6 29
2662 0	353 2	0 371	∞	380 2		4096	365 3	6 18
5324 0	368 3					∞	379 2	
∞	385 9							

Cyanoacetic acid		o Chlorobenzoic acid		o Nitrobenzoic acid	
Dilutions	λ_o	Dilutions	λ_o	Dilutions	λ_o
20 80 and 41 60	302 2	150 01 and 300 2	251 7	32 and 64	356 1
83 20	350 1	600 4	348 9	128	362 3
166 4	361 0	1201 0	340 3	256	367 4
332 8	370 4	2402 0	357 9	512	372 2
665 6	377 5	4804 0	368 5	1024	375 5
1331 0	380 5	9608 0	374 2	2048	377 4
2662 0	383 4	300 2 and 600 4	379 8	4096	378 0
5324 0	384 7	1201 0	379 5	64 and 128	364 2
41 60 and 83 20	357 4	2402 0	380 2	256	369 3
166 4	366 6	4804 0	380 3	512	373 6
332 8	374 2	9608 0	380 4	1024	376 3
665 6	379 8	600 4 and 1201 0	380 4	2048	377 0
1331 0	382 8	2402 0	379 7	4096	378 3
2662 0	384 2	4804 0	380 3	128 and 256	372 1
5324 0	385 2	9608 0	380 4	512	375 4
83 20 and 166 4	372 3	1201 0 and 2402 0	379 4	1024	377 4
332 8	378 1	4804 0	380 3	2048	378 4
665 6	382 4	9608 0	380 4	4096	378 5
1331 0	384 2	2402 0 and 4804 0	380 8	256 and 512	377 3
2662 0	384 9	9608 0	380 6	1024	378 4
5324 0	385 6	4804 0 and 9608 0	380 5	2048	379 0
166 4 and 332 8	381 6			4096	378 8
665 6	384 6			512 and 1024	379 1
1331 0	385 4			2048	379 3
2662 0	385 5			4096	379 0
5324 0	385 9			1024 and 2048	379 3
332 8 and 665 8	386 3			4096	378 9
1331 0	386 0			2048 and 4096	378 7
2662 0	385 8				
5324 0	386 1				
665 8 and 1331 0	385 9				
2662 0	385 8				
5324 0	386 1				
1331 0 and 2662 0	385 8				
5324 0	386 1				
2662 0 and 5324 0	386 3				

form here discussed, if measurements can be made, on solutions sufficiently dilute, with the necessary degree of accuracy. It is interesting, therefore, to apply the criterion of "calculated" λ_0 to such electrolytes which have been so carefully measured, these results are given in Table V, as calculated from the data given by Kendall.

Since Kendall finds that, at and below a certain concentration, constant values are obtained for the mass law constant, it would be expected that a similar behavior would be found in the values for "calculated" λ_0. For each acid given in Table V, it is seen that the values for "calculated" λ_0 regularly increase to a constant maximum value. This increase in value should be steady for increasing dilution or decreasing concentration and never fluctuate from greater to lesser to greater, etc., values. If such is the case, the criterion, "calculated" λ_0, demonstrates the lack of precision due to errors in the measurements. The extreme sensitiveness of the criterion detects such errors even in the very accurate data of Kendall for o-chlorobenzoic acid given in Table V. The application of "calculated" λ_0 as a test of the precision of the conductance data of transition electrolytes is, therefore, obvious.

To detect the presence of constant errors, the average maximum constant value for "calculated" λ_0 must be compared with the value for λ_0 obtained independently by the salt method as shown under Section II. If no maximum constant value is obtained in any given case, it is obvious that the conductances of more dilute solutions must be measured, but for most organic electrolytes it will be unnecessary to measure solutions more dilute than o.ooo5 N. A graph, obtained by plotting λ_0 as ordinates against the dilution as abscissae will often give much information concerning what dilutions must be measured in order that constant values for "calculated" λ_0 may be obtained. However, this graphic method will not give the correct value for "calculated" λ_0, since a range of dilution is employed in its calculation. The application of this criterion of constant errors to the data of Table V is given in next section.

V. A Simple and Accurate Method for the Determination of the Molar Conductance at Zero Concentration of Organic Electrolytes.

In Section I it was shown that electrolytes of the strength of acetic acid obeyed the ideal mass law in the form $k = C\lambda^2/\lambda_0(\lambda_0 - \lambda)$ for all concentrations below o.o2 N, within the error of the present measurements.

In Section II it was shown that the molar conductance of such electrolytes at zero concentration could be calculated from any two values of its molar conductance at two different concentrations, provided such concentrations are below o.o2 N, with the same degree of accuracy with which this value can be determined by the salt method, and in fact to a much

The same facts are true of the conductance of the salt of the organic acid at zero concentration as for the cation. Hence in the value for λ_0, by the salt method, the water correction is of slight importance in comparison to this value when calculated from the conductance of the organic acid. Further, the question of the application of the water correction to salts has been fairly well agreed upon and it is usually applied, so that the only uncertainty which surrounds this correction to the λ_0 value by the salt method is its application to the conductance of the strong acid (hydrochloric acid), from which the mobility of the hydrogen ion is obtained, where it is of minor influence, however

The very accurate work of Kendall discussed in this paper shows that *no water correction should be applied to his data upon transition electrolytes if the specific conductance of the water is less than 0.9×10^{-6}*, since his uncorrected data give "calculated" λ_0 values which agree with the values obtained by the salt method with an accuracy greater than 0 1% in the dilute solutions. Kendall found that he obtained a better constant for the mass law using his uncorrected data and, therefore, chose this data as the most accurate, which choice is justified by the application of the criterion "calculated" λ_0 in this paper.

To realize what influence the water correction has upon the ionization constant and upon the criterion "calculated" λ_0 the following tables have been compiled, using Kendall's data upon acetic acid discussed in Section I of this paper. In Table VI, Column I gives the dilution (v) of the measurement, II the corrected specific conductance ($\underline{L}^c$), III the corresponding uncorrected specific conductance ($\underline{L}^u$), IV the percentage influence of the water correction, V and VI the ionization constants for the uncorrected (k_a^u) and corresponding corrected data (k_a^c). Table VII gives the "calculated" λ_0 values for the corrected (λ_0^c) and corresponding uncorrected (λ_0^u) data.

Table VI shows that the uncorrected data for the conductance of acetic acid give far more satisfactory ionization constants than the corrected data and that, even though the water correction is 1.69% of the total uncorrected specific conductance, it should be entirely neglected if acetic acid approximates the mass law within 0.1%.

Table VII shows that acetic acid does closely approximate the mass law and that the correction for the specific conductance of the water should be neglected entirely for all concentrations for the data measured by Kendall. A comparison of the corrected and uncorrected ionization constants of acetic acid from Table VI with the corresponding corrected and uncorrected values for "calculated" λ_0 from Table VII shows how much more sensitive the latter values are as a criterion of the precision of and constant errors in the conductance data for weak electrolytes. Numerous other

TABLE VI

v	$L^c \times 10^4$	$L^x \times 10^4$	$L^u_{H_2O}$	$k_a^u \times 10^8$	$k_a^c \times 10^8$
13 57	4 476	4 485	0 204	1 845	1 839
27 14	3 156	3 165	0 284	1 851	1 839
54 28	2 218	2 227	0 404	1 849	1 833
108 56	1 555	1 564	0 575	1 849	1 826
217 1	1 088	1 097	0 820	1 851	1 821
434 2	0 7561	0 7651	1 17	1 849	1 804
868 4	0 5222	0 5312	1 69	1 850	1 784
1737 0	0 3571	0 3661(5)	2 46	1 854	1 754
3474 0	0 2406	0 2496	3 60	1 855	1 706
6948 0	0 1592	0 1682	5 35	1 870	1 639

TABLE VII

Dilution series v and v_1		Calculated λ_0		Dilution series v and v_1		Calculated λ_0	
		λ_0^u	λ_0^c			λ_0^u	λ_0^c
13 57 and	27 14	766	443 0	108 56 and	217 1	551	338 6
	54 28	449	341 1		434 2	434	303 2
	108 56	359	319 6		868 4	414	307 8
	217 1	416	326 7		1737 0	408	306 0
	434 2	402	313 8		3474 0	401	302 2
	868 4	399	325 4		6948 0	403	301 7
	1737 0	399	308 0	217 1 and	434 2	379	293 6
	3474 0	396	304 0		868 4	388	300 3
	6948 0	400	302 8		1737 0	393	301 7
27 14 and	54 28	348	294 0		3474 0	392	299 4
	108 56	311	296 0		6948 0	398	300 0
	217 1	389	314 1	434 2 and	868 4	394	304 9
	434 2	384	305 5		1737 0	398	304 0
	868 4	388	313 4		3474 0	394	300 4
	1737 0	532	304 6		6948 0	400	300 5
	3474 0	391	301 7	868 4 and	1737 0	400	303 3
	6948 0	458	301 3		3474 0	381	299 2
54 28 and	108 56	290	297 3		6948 0	401	299 9
	217 1	402	320 4	1737 0 and	3474 0	390	296 7
	434 2	391	306 7		6948 0	401	299 0
	868 4	392	306 4	3474 0 and	6948 0	409	300 4
	1737 0	395	305 2	λ_0 by the salt method =			387 7
	3474 0	393	301 9				
	6948 0	399	301 5				

measurements in this laboratory, which will be published shortly, confirm Kendall in neglecting entirely the correction for the specific conductance of the conductivity water   The advantage of this method in determining the question of the application of the water correction is that it is applicable to the given solution of a weak acid under the ordinary conditions of measurement and necessitates no other procedure than a simple calculation.

URBANA, ILL.

ELECTROLYTIC ENDOSMOSE.

BY HORACE G. BYERS AND CARL H. WALTER.

In 1901, F. J. Parker presented a thesis "In Partial Fulfilment of the Requirements for the Doctor's Degree," which has not otherwise found publication, in which he details the results of certain experiments with a tripartite cell involving electrical endosmose. These results are of a character which held a high degree of interest for one of the present writers and have led to the present investigation. The experiments here detailed represent the beginning of what we hope may develop into a much more extended series which may be of value. We shall, therefore, attempt to present first an historical résumé of the subject with a bibliography which, if incomplete, may be extended in subsequent papers.

Historical.

Apparently the first observation of electrical endosmose was by Reuss,[1] who observed the transfer of liquid from one side of a porous clay membrane to the other during the process of electrolysis. Similar observations were made by Poiret, Becquerel, Armstrong and Daniels with other membranes. The first careful study of this transfer of water during electrolysis was made by Wiedman[2] and by Quincke.[3] The general results of these observations may be summarized as follows:

When a liquid, separated into two portions by a porous septum, is subjected to electrolysis, the flow of liquid through the septum is proportional to the intensity of the current, the specific resistance of the liquid and the thickness of the membrane, and inversely proportional to the porosity of the membrane. The direction of the flow with electrolytes is generally with the current, i. e., toward the cathode, but under certain circumstances the flow is contrary to the current. No further contribution to the experimental side of the subject appears to have been made until 1898, when Alfred Coehn[4] showed that during the progress of endosmose the liquids and the diaphragm became electrically charged and in different liquids with charges of opposite sign.

In 1900, J. C. Olson[5] accidentally encountered electrical endosmose in the preparation of permanganic acid from potassium permanganate by electrolysis, using a porous clay cup as a means of separation between anode and cathode. In attempting to improve upon his method, F. J. Parker[6] made use of two cups, one containing the anode and the other the

[1] *Mem. de la Soc. imp. des Nat. de Moscow,* 11, 332 (1808).

[2] *Pogg. Ann.,* 87, 321 (1852).

[3] *Ibid.,* 107, 1˝(1859); 110, 38 (1860); 113, 513 (1861).

[4] *Wied. Ann.,* 64, 217 (1898); 66, 1191 (1898).

[5] *Am. Chem. J.,* 23, 431 (1900).

[6] Johns Hopkins Dissertations, 1901.

cathode. He says: "Electrical endosmose in these experiments proceeded simultaneously in both cups in *opposite* directions."

In 1903-4, Jean Perrin[1] published an exhaustive account of many experiments. In these he used very thick membranes, 10-12 cc., made of a large variety of substances. He found, in general, that all membranes behaved alike in respect to the charge assumed by it and that, in general, the direction of flow of water during electrolysis was with or against the current according to the charge assumed by the membrane. Apparently this charge was positive or negative according as hydrogen or hydroxyl ions were in excess in contact with the membrane.

In 1902, Reed,[2] in a paper designed to point out errors in the determination of migration ratios, called attention to a case of endosmose in which the solvent migrated toward neither electrode but apparently away from both. Certain experiments with the apparatus designed by him are described in this paper.

Bancroft[3] advances, in a discussion of the work of both Perrin and Reed, an explanation of endosmose which is essentially that the direction of flow is determined by the relative adsorption of the ions of greatest concentration.

It will be observed that in the explanations offered by Wiedeman, Perrin and Bancroft, note is taken of the electrical charges on the porous septa. No explanation is furnished for the transfer of water through the septa. It does not appear to have been realized that water may be transmitted through septa, under varied conditions, either with or against the direction of the current, in both directions at the same time, or away from both electrodes. In this paper instances of all these kinds are described and also an instance where it is apparent that water not only migrates with the current but flows more rapidly away from the anode than to the cathode.

Before presenting the experiments, we also desire to call attention to the work of Washburn, which itself presents a summary of previous work on the hydration of ions. In his paper Washburn[4] demonstrates that water is carried with the cathions of hydrogen and the alkali metals into the cathode chamber of a migration ratio apparatus specially designed for the investigation. This Washburn takes to be a demonstration that these ions are hydrated. The work of Washburn was repeated in this laboratory and the observations extended to the chlorides of the alkaline earth metals.[5]

[1] *Compt. rend.*, 137, 513 (1903); *J. chim. phys.*, 2, 601 (1904).

[2] *Trans. Am. Electrochem. Soc.*, 2, 238 (1902).

[3] *Ibid.*, 21, 233 (1912).

[4] THIS JOURNAL, 31, 322 (1909).

[5] The work has not been published except as a Master's thesis by J. M. McGee.

Bartell[1] in an article on negative osmose, describes a series of experiments in which he obtains *concentration* of solutions by transfer of water through clay membranes into the pure solvent. The bearing of these papers on the subject of the paper will be pointed out in our conclusions.

Before passing by the literature of the subject, attention may be called to the fact that industrial application of endosmose is being attempted and the various plans are covered by patents among which are German patents 124,509, 128,085, 239,649, and English patents 3,364 and 11,626.

Experimental.

In the experiments described below, the apparatus first used was a simple tripartite cell, consisting of two battery cups of ordinary type, set in a battery jar, and kept about a quarter of an inch apart (Fig. 1).
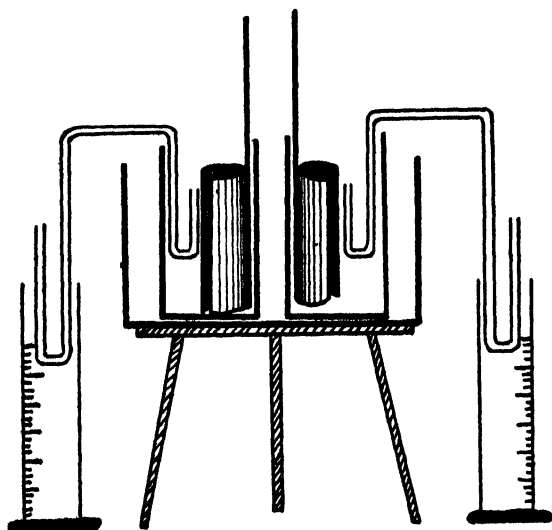
Fig 1.

In each cup was placed a platinum electrode 100 × 50 mm. and an intermittent syphon, so that any rise in the level of the liquid would cause an overflow into a suitable graduated vessel. Before beginning an experiment, the whole apparatus was filled with the solution to be examined and when in the course of an experiment the level of liquid in the battery jar tended to fall materially, its level was maintained by addition of the original solution from a reservoir through a dropping siphon. In this apparatus nine solutions and a total of twenty-two experiments were performed. The results are given in Table I.

Attention is directed to the following points illustrated by the table:

The first four experiments show the verification of Parker's work, and that both anode and cathode flow takes place at various dilutions. The walls of both cups become more or less clogged with reduction products of the permanganate. Similarly, flow in both directions occurs with

[1] THIS JOURNAL, 36, 646 (1914).

TABLE I

	Solute.	Solvent	Solution	Amperes	Volts	Kathode flow Cc	Anode flow Cc	Time in hrs	Temperature Initial-Final
1	KMnO₄	Water	Saturated	2 -1 4	26-52	212	40	5 30	22-55
2	MKnO₄	"	20 g -L	2 -1 3	32-54	560	103	5 30	20-57 5
3	KMnO₄	"	10 g -L	2 -2 0	68-42	1565	265	5 10	21-56
4	KMnO₄	"	1 g -L	0 4 -1 2	106-108	3000	210	5	18-60
5	KClO₃	"	20 g L	2 -1 2	13-35	265	62	8 10	28-48
6	KClO₃	"	20 g -L	2 -1 3	87-70	295	58	5	21-59
7	KClO₃	"	10 g L	2 -1	33-72	900	160	7 30	26-54
8	NaCl	"	20 g -L	2 -2 2	20-9 5	125	100	8 10	24-38
9	CuSO₄	"						0 15	10-34
10	CuNO₃	"	Normal	2 -0 5	86-102			2	10-34
11	Na₂SO₄,10H₂O	"	⅓ N	2 -2 0	42-10	55	0	6	9-17
12	Na₂SO₄,10H₂O	"	½ N	2 -2 0		60	0	6	45-50
13	Borax	"	Saturated	2 -	34-	10	0	0 08	20-32
14	Borax	"	Saturated	2 -1	32-78	500	0	3 18	20-38
15	K, alum	"	Saturated	2 -0 2	48-120	0	0	7 20	21-36
16	K, alum	"	1/1000 sat	0 025-0 005	108-110	85	75	8 30	19-24
17	K, alum	"	1/1000 sat	0 050-0 006	101-110	425	0	9 00	21-23
18	K, alum	"	9/1000 sat	0 023-0 006	110-110	500	16	6 30	19-24
19	FeCl₃	"	Sp gr 1 070	2 -0 4	12-0	0	20	2 40	18-34
20	FeCl₃	"	Sp gr 1 070	2 -0 4	0 6-120	0	22	6 45	20-60
21	FeCl₃	"	Sp gr 1 070	0 09 -0 09		0	0	8 30	17-21
22	FeCl₃	"	1/1000	22 6 -0	100-0	0	45	4 00	16-17

potassium perchlorate. When sodium chloride is used no anode flow takes place at first, and indeed, in one experiment for three hours, while at the end of the experiment the anode flow is approximately five drops to one at the cathode. It is probable that perchloric acid, formed at the anode, is the cause of the flow but no attempt was made to determine its quantity.

Copper sulfate shows no tendency toward flow toward either cathode or anode, but at the end of fifteen minutes the current automatically disconnected itself, due to recession of liquid from *both* cups. Copper nitrate shows lowering of level in the cathode compartment alone.

Since in all the previous cases the electrolysis caused considerable rise of temperature, in the next case (11) the solution of sodium sulfate, hydrated, was kept in a cold water bath to prevent decomposition of the hydrate. Yet under these circumstances, as well as where the temperature was allowed to rise, only slight cathodic flow is to be observed. In Expt. 13, with a saturated borax solution, within eight minutes, the solutions had receded from the anode cup so rapidly as to break the circuit, indicating a flow of about 100 cc., while an increase of only 10 cc. had taken place in the cathode cup. This seemed a good case with which to ascertain whether acidity causes anodic, and alkalinity, cathodic flow. Expt. 14 was conducted exactly as thirteen except that in the anode cup was placed a mixture of borax solution and concentrated sulfuric acid. No change in the level of the anode cup was observed, though 500 cc. passed from the battery jar into the cathode cup.

Experiments with potassium alum (15, 16, 17, 18) show very interesting variations. In a saturated solution there occurred a very slight cathodic flow and then a fall in both cups, though in neither to an extent to disconnect the current. The cathode cup became coated on the *outside* with a deposit of aluminium hydroxide and finally showed a static charge of sufficient intensity to give sparks when touched above and below the liquid surface. This is evidently a marked case of stenolysis. With the formation of the hydroxide the resistance rises markedly with consequent fall of current.

With 0.001 N alum solution, the solution fell at first in both cups and then began to rise, but while the anode cup slowly overflowed no rise took place in the cathode cup for six hours, after which it flowed so rapidly that in two and a half hours more the total flow exceeded that of the anode. Seventeen and eighteen are attempted duplicates of sixteen.

In several experiments not included in the table, the acidification of the cathode cup with dilute sulfuric acid, stopped the flow, while making it alkaline increased it. Acidification of the anode cup had the opposite result.

In the experiments with ferric chloride, uniform results are secured

and only anodic flow is noted. Yet the flow *from* the cathode cup is so marked that to keep from disconnecting the current solution must be continually added. In Expt. 19, 220 cc. were added to the cathode while only 20 cc. passed into the anode cup. The iron deposited at the cathode was apparently pyrophoric. In Expt. 21, with only 90 m. amp. current, no flow occurs in either cup. In Expt. 22, while only 45 cc. overflow occurs in the anode cup, 280 cc. had to be added to the cathode.

Manganese chloride and magnesium chloride also show only negative flow, and *from* the cathode cup in excess of that *into* the anode cup. The results due to formation of oxides were variable and no definite figures are given.

In order to study these phenomena more closely, two pieces of apparatus[1] were prepared as illustrated in Fig. 2. The membranes were made of
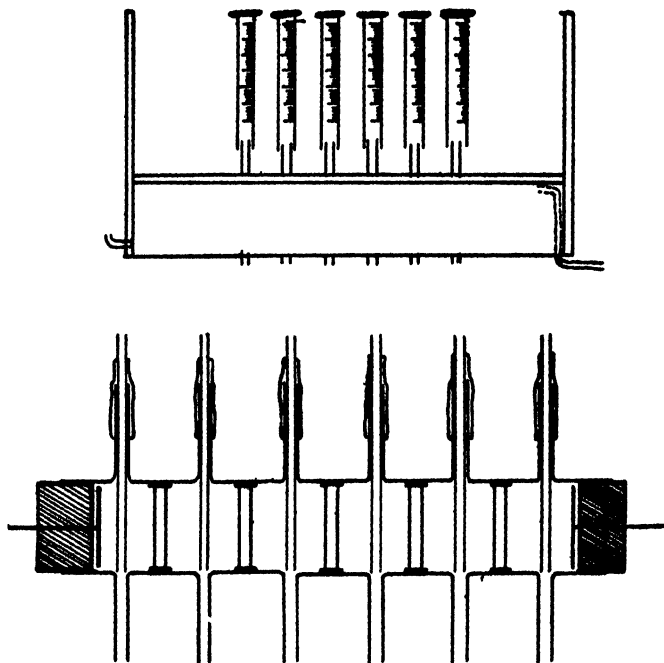
Fig 2.

ordinary unglazed plates and were ground to a thickness of 2 mm. Each compartment was provided with an automatic overflow by tubes held in position by rubber tubing. The whole apparatus was placed in a trough through which tap water was continually running. The electrodes

[1] After Reed, *Loc. cit.*

were either coiled platinum wires or platinum plates inserted in rubber stoppers. In running this apparatus the chief difficulty is caused by stenolytic deposits in the plates, the removal of which, with assured completeness, is nearly impossible. In detailing experiments, the compartments are numbered from the anode end.

One experiment, which could not be duplicated, has special interest. The apparatus was filled with a saturated alum solution and electrolysis begun with a current of 30 m. amp. and 120 volts. A miniature tidal wave moved from compartment one through two until six was reached, a small overflow taking place in each. The tide then turned, and starting from six, the wave flowed back, filling each partly emptied compartment, until "one" was again full. The wave then started on the reverse path, but the double turn had consumed about ten hours and, due to stenolytic deposit, the current had fallen to 5 m. amps. and the transfer of liquid was very slow. The experiment was discontinued and, when repeated, similar results were not obtained.

The results obtained with this apparatus verified in general those obtained in the tripartite cell. A careful study was made of the behavior of ferric chloride. Overflow took place as indicated in Table II, in four series of experiments. In Series 1, 2 and 3, the solution was ferric chloride of specific gravity 1 070 and in 4 the same solution diluted ten fold.

TABLE II.

Expt.	Time. Hours	1 Cc	2 Cc	3 Cc	4 Cc	5 Cc	6	Current. M. a
1......	7	5 0	1	0 6	1 8	15 0	0	325
2.....	5¼	9 0	0	0 4	1 3	7 0	0	325
3. .	7	6 0	0	0	0 8	20 0	0	325
4. ..	5	10 0	1	2 0	1 5	16 0	0	150

The plate between compartments 5 and 6 showed granular nodules of metallic iron on the side toward the anode pole. There was also liberation of chlorine from compartments 5 and 6 as well as from 1. These results are clearly due to stenolytic decomposition. Considerable color change also accompanied the process of electrolysis as is to be expected, but apparently no connection exists between the color and iron content. No attempt was made to determine the relative quantities of ferrous and ferric iron. At the end of each run the contents of each compartment were withdrawn and added to the overflow, if any. The iron from compartments 5 and 6 was dissolved, except as noted in the table, and also added. The total quantity of iron in each compartment liquid was then determined, after reduction with stannous chloride, by titration with permanganate. The results are indicated in Table III, calculated per cc. of solution. The value of the original solution in iron is 0.03498 gram per cc. for 1, 2 and 3 and 0 003498 for No. 4.

Comp.	Run 1.	Run 2.	Run 3.	Run 4.
1	0.0187488	0.016202	0 0169632	0.0024552
2	0.031649	0.045756	0.0308016	0.0035712
3	0.0316154	0.0310248	0.0319396	0.0036828
4	0.0305226	0.0325314	0 0319396	0.003906
5	0.023591[1]	0.0275652	0.0325872	0.0040176
6	0.040979	0 0479322	0 0465372	0.0074772

A set of readings of galvanometer deflections produced when the instrument was connected with wires leading from opposite sides of each of the plates was also taken, for experiment marked above, Run 1, but aside from indicating that the opposite sides of each plate had different potentials at the end of the experiment, no value is to be attached to the same and the data obtained are omitted.

Summary and Conclusions.

The following facts are illustrated by the foregoing experiments:

1. Endosmose is capable of producing flow of electrolytes in the direction of the current, in the opposite direction and in both directions at the same time.

2. In certain cases the flow of electrolyte is away from both electrodes and also may be more rapid away from one than to the other; in either case the content of the middle compartment of a tripartite cell is increased.

3. In the six-compartment cell the change in volume is not confined to the anode and cathode compartments, but varies in the other compartments in an apparently erratic manner.

4. The quantity of water transported is clearly affected by the dilution of the electrolyte.

5. When clay membranes are used, the endosmose is complicated by stenolysis.

Far-reaching conclusions of a theoretical nature are not to be drawn from the meager data submitted in this paper and, since there seems to be a more or less intimate connection between these observations and the questions of molecular and ionic hydration in solution, negative osmosis and migration ratios, as well as the question of endosmose itself, the work will be continued in the hope that more accurate and valuable results may be obtained.

In the meantime it does not appear clear to the writers how electrical charges upon the plates induced by varying degrees of ion adsorption or otherwise accounts for the *traversal* of the plates by water.

UNIVERSITY OF WASHINGTON.
SEATTLE, WASH.

[1] Iron on electrode not dissolved.

THERMOELEMENTS OF PRECISION, ESPECIALLY FOR CALORIMETRY.

By WALTER P. WHITE.

The advantages of the thermoelement for calorimetry and similar work of high precision have been briefly stated, and the design and arrangement of the potentiometer and other auxiliary apparatus have been described in other papers of this series.[1] The construction and use of the thermoelement itself are simple matters, yet variations, apparently slight, in design or procedure may make great differences in the labor required or the success attained. The present paper aims to treat these details more explicitly than has yet been done, as well as to present some new material.

The thermoelement is merely a bundle of suitably connected wires, and the only problems presented by its construction concern, first, the quality of the wires, and second, their insulation and protection.

I. Multiple Elements.

The simplicity of the thermoelement has this consequence: that it is about as easy to have a considerable number of wires with, of course, a corresponding gain in sensitiveness, as to use a single pair. The use of many junctions has indeed been the rule in thermoelectric apparatus generally, but in thermometric work it has been customary to employ a single couple, and the use of more has often been regarded as a matter for special mention.[2] Convenience evidently dictates exactly the opposite procedure; it is the single couple which should not be used without special reason. The number of couples which can be installed as easily as one will generally be from four to twelve, according to circumstances; with thermo-

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[1] This Journal, 36, 1859, 1876, 2011 (1914).

[2] *Nomenclature.*—The classic division of all thermoelectric apparatus into thermocouples and thermopiles is unfortunate. It classes together instruments of widely different nature and use, and lays a most inconvenient emphasis on the usually trivial distinction which comes from the number of parts. A "thermopile" is still a thermopile, whether it does the work of a dynamo, of a radiometer, or of a thermometer, but it must change and become a "thermo*couple*" whenever a single pair of metals happens to be used. What is wanted is, evidently, to have terms each of which applies to the instruments of one kind and applies to all of them. The term "Thermoelectric Thermometer," analogous to "Resistance Thermometer," is such a term. Its length, however, seems likely to prevent its general adoption; it will scarcely displace the word "thermocouple" in cases where the latter is now properly in use. But the general practice of using a single pair of metals for thermometric work has brought it about that while the word thermopile naturally suggests other than thermometric uses, the term thermoelement suggests nothing else. It therefore seems practicable to use "thermoelement," as a familiar, intelligible and convenient synonym for "Thermoelectric Thermometer." "Multiple" and single thermoelements can then be discriminated (when necessary) without concealing their essential similarity.

elements of from 25 to 100 couples, the very great precision reached is obtained at the cost of some, not serious, inconvenience.

II. Quality of the Wire.

The thermoelement, in itself, has only two sources of error: defective insulation, and inhomogeneity of the wires composing it. Of these, inhomogeneity is of course the only one peculiar to the thermoelement. Formerly a frequent cause of serious error, and still troublesome at very high temperatures, it can easily be rendered harmless in calorimetric and similar work. To this end, however, it is of course well that the maker, and to some extent the user, of the thermoelement should understand the nature of the effect which inhomogeneity produces.

1. General Law of the Inhomogeneous Thermoelement.—From the elementary facts of the thermoelectric circuit, it follows that any thermoelement may be taken as equivalent to a number of similar but shorter ones placed end to end, each measuring the temperature difference between its own terminals.[1] The most effective of these partial thermoelements, that is, the effective portions of the real thermoelement, will then be those lying in the steepest temperature gradients. Thus in Fig. 1, if A B C D E represents the temperature distribution along the thermoelement *a b c d e*, the resulting electromotive force (that is, the reading) will depend mainly on the quality of the wire *bc*, lying in the gradient B C; the portions *ab* and *ce* will have only a secondary effect. *If the gradient shifts from B C*

Fig. 1.

to C D the effective thermoelement will be changed; it will be no longer the portion bc but cd.
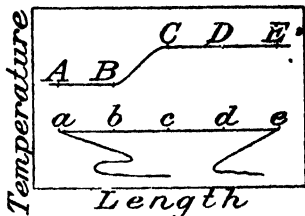
It follows that a thermoelement will be strictly constant if it is either perfectly homogeneous, so that its various portions may be indifferently substituted for each other, or else is always used with the temperature gradients in the same places; and evidently, if both these conditions are partly fulfilled neither will need, in practice, to be fulfilled completely. This is emphatically the case with calorimetric thermoelements, where the original quality of the wire is often sufficient in itself to give all needed precision, and where the gradients are also very steady.

It also follows that in any thermoelement the quality of the wire not in the temperature gradients is of less or no importance. This nearly always applies especially to the portions near the junctions,[2] a point of

[1] The demonstration occurs in: "The Thermoelement as a Precision Thermometer," Walter P. White, *Phys. Rev.*, **31**, 135–40 (1910).

[2] Since there cannot be any considerable temperature gradient near the junction, if the junction is to be at the temperature of the medium whose temperature is being measured.

great practical importance which has often been overlooked by users of thermoelements.

2. *Inhomogeneity in Particular Cases.*—The way in which inhomogeneity may affect different forms of the thermoelement is easily seen from the above.

(a) *Thermoelement Wholly within the Jacket.*—The simplest arrangement is where the thermoelement is wholly inside the calorimeter jacket, and runs to a second calorimeter. The total temperature gradient is then no greater than the temperature change which is to be measured. This gradient will always be at about the same place on the thermoelement; at the worst it will not shift by more than one-fourth its own length, that is, from *ac* to *bd* in Fig. 2. This is evidently equivalent to shifting one-fourth of the gradient from *ab* to *cd*, leaving three-fourths unchanged in *bc*. If we suppose that the maximum variation in thermoelectric quality is 100 per million—a high value with present methods of construction—and, moreover, that all of it exists between *a* and *c*, the uncertainty due to the shift of the gradient would be one-fourth of 0.000100, or 0.000025.
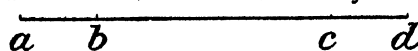
$$a \quad b \qquad\qquad c \quad d$$

Fig. 2.

It is worth noting that the absolute value of this error would diminish with the interval. A resistance thermometer, for instance, which when at its best reads to 0.0001°, would indicate an interval of 4° as accurately as this rather inferior thermoelement, and a larger interval more accurately, but for an interval of only 0.1°, while the precision obtained with the resistance thermometer would have fallen to 1 per mille, the thermoelement would still be good for 0.025 per mille (or 0.0000025°) as far as any error due to inhomogeneity is concerned, and would be limited practically only by the delicacy of the electrical reading.

(b) *Thermoelement Partly Outside the Jackets.*—If the middle of the thermoelement is directly exposed to the air of the room, there will be at each end of the exposed portion a gradient whose value will change as the room temperature changes. If the wire lying in these two gradients differs in quality, any change of room temperature occurring during a determination will cause an error. If this error seems likely to be appreciable it can easily be prevented by shielding the exposed (horizontal) portion of the thermoelement with an inverted trough of sheet copper, which straddles it and dips into the jacket water on each side. With such a temperature-controlling shield made of copper 0.8 mm. thick, reaching 36 mm. above the water and 14 mm. wide at the top, the maximum variation from the temperature of the water was only 0.04 of the difference between water and air. When two such pieces of copper were used, one over the other, separated by a little blotting paper, the maximum variation on the inner one was below 0.02 of the water-air difference.

With this simple arrangement in use, then, the room temperature would have to change over $40°$ in order to produce an error of 0 0001°, even with the rather inferior thermoelement supposed above. With full exposure of the middle of the thermoelement to the open air, however, a change of $3°$ in room temperature might produce an appreciable effect in any but the most homogeneous thermoelement. Hence such an exposure should not be practiced in work of high precision, particularly since the prevention of it is so very easy.

(c) *Thermoelement with Ice Bath.*—If one end of the thermoelement, instead of being in a second calorimeter, is in an ice bath, there will be introduced a gradient of $20°$ or so, with an error in case the gradient shifts which may possibly be 0 001° but more probably as low as 0 0002°. To avoid this error, time must be allowed for equilibrium to set in after inserting the thermoelement. After that, changes due to inhomogeneity will be very slight and slow, and probably no greater than those which may result from small changes in the temperature of different portions of the bath itself. But the ice bath is not recommended for calorimetric work of the highest precision, and it is one important advantage of the methods here presented that they avoid its use.

(d) *Adiabatic and Non-adiabatic Methods.*—In adiabatic methods the gradient occurs at the outer edge of the jacket. If, therefore, the same arrangement is used, sometimes for adiabatic and sometimes for non-adiabatic methods, the effective thermoelement is not the same in the two cases, and the results may differ a little. The difference, however, is usually quite negligible and is, moreover, easily determined, but the possibility of its occurrence should not be wholly overlooked.

3. Selection and Testing of Wire.—Commercial copper wire is sufficiently homogeneous for precision thermoelements. Methods have been described for arranging inferior constantan wire so as to secure a very satisfactory resultant homogeneity.[1] These effective but relatively laborious methods are no longer necessary. Our study of this earlier wire convinced us sometime ago that the production of satisfactorily homogeneous constantan wire was easily possible, as soon as any manufacturer should become sufficiently interested to undertake it. The Electrical Alloy Company, of Morristown, N. J., at our request, have furnished several samples of "specially annealed" wire[2] which confirm this view. Although the 200 meters and more which have been tested contain a few (relatively) bad spots, they consist mainly of continuous stretches of wire varying less than 0.0007 in thermoelectric power against copper and therefore

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[1] "The Constancy of Thermoelements," Walter P. White, *Phys. Rev.*, **23**, 470 (1906); "The Thermoelement as a Precision Thermometer," *Loc. cit*, 140–43.

[2] Their trade name is "Ideal," but the wire is practically the same as Constantan (40% nickel).

good enough to make, without any further selection or arrangement, thermoelements precise to better than one-ten-thousandth.[1]

It is of course possible that an occasional spool might consist mainly of inferior wire. If three samples distributed through a spool are all inferior it will probably be best to send for another spool, since the cost of the untested wire is a trifle. In general, however, judging by past experience, the chances are over 10 to 1 that any particular 30-meter length will contain much good wire, and work now in progress will probably soon render the situation still more satisfactory.[2] Meanwhile, the testing of enough wire for a very sensitive thermoelement will seldom prove long or laborious.

4. *Sizes of Wire.*—In general, it is desirable that the thermal conductance of a thermoelement should be small, the electrical conductance large. It is easy to show that the ratio of electrical to thermal conductance is a maximum when the ratio of the cross sections of the two kinds of wire, 1 and 2, equals $\sqrt{\frac{\sigma_1 \kappa_1}{\sigma_2 \kappa_2}}$, where σ is the electrical, κ, the thermal, conductivity. For copper and constantan this calls for a ratio of about 21.4 to 1 at 18°. A somewhat smaller ratio will do nearly as well, if it is desirable for mechanical or other reasons, but it is clear that very inefficient ratios have often been used. For the constantan, 0.25 mm. diameter (No. 30 B & S) is about the most convenient size in the great majority of cases.

5. *Method of Testing.*—The essential feature of all methods of testing wire thermoelectrically is to heat (or cool) successively various portions of the wire, and observe the electromotive force produced. This electromotive force at any instant measures the difference in thermoelectric power between the two ends of the heated portion. The most obvious method is to draw the wire *through* a warmed bath or tube. In that case both gradients are changing at the same time, and the interpretation of the observations is usually troublesome and unsatisfactory. The method will, however, distinguish readily enough between wire which is wholly free from irregularity and that which is not, and has been used in making some excellent thermoelements, by rejecting altogether all wire which was not clearly excellent.

It is about as easy, however, to secure more complete information,

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[1] Our last spool received shows, as far as tested, 99% of wire varying less than 0.0002, and considerable wire as good as this has been obtained from other spools.

[2] The difficulty lies in our present ignorance as to the causes of the inhomogeneities sometimes found in carefully made constantan wire. Some preliminary work on the problem failed to give definite results, and thus showed that the problem has sufficient difficulty to be probably worth while as a research. At the same time the number of factors is so small that a successful solution could be confidently expected, and its practical usefulness would be considerable. It is to be hoped that some one will take the matter up.

often resulting also in a greater economy in using the wire, by drawing the wire *out of* a heated bath, leaving one end of the heated portion unchanged during the test. All other parts of the wire, as they are successively drawn out of the heated region, are then compared with the unchanging part, and a complete map of the variations of the whole is thus obtained. It is important to be able to handle the wire readily without snarling or kinking; this can be done by running it from one drum to another, putting one of the drums in the heated bath. If the wire is insulated, as it usually will be if intended for multiple thermoelements, it is more simply and surely tested if in one single piece. The two ends then run from the drums to copper leads, which run to a sensitive galvanometer. Twisting of these portions as the drums turn is prevented by letting them wind (or unwind) about the slender axles of the drums; the small amount of wire which is thus coiled to a small radius is thrown away after the test. The wire is best brought out of the hot bath along the axle of the drum and allowed to make its small coil above in the air, where it can be easily attended to. (This is an improvement over previous published methods,[1] and was suggested by Mr. L. H. Adams of this laboratory.) Two strips of sheet copper wound around the axle, one at the surface of the liquid and the other a little higher, will keep the gradient, which will be mostly between them, constant as the drum turns.

The E. M. F. of a copper constantan couple for 80° temperature difference is over 3000 microvolts, hence in this test an irregularity of 2 microvolts is enough to cause rejection of the wire; the readings must therefore be good to a microvolt or better, and the galvanometer must accordingly be arranged for eliminating the effect of parasitic thermal forces.[2] The galvanometric precision, however, may always be less than is to be used in reading the thermoelement after it is made. The parasitic E. M. F.'s produced by ordinary irregularities of the air temperature and of the bath are of course quite negligible, when eighty degrees produce only a microvolt or two. The junctions to the two copper leads, however, must not differ by more than 0.005°. If other means fail, they can easily be kept as near as this by putting them together into a stirred bath at room temperature. The equality of temperature can be tested by seeing how nearly the galvanometer reads zero before the hot bath is heated.

The hot bath can be conveniently filled with kerosene at 100°. The wire, even when wet with kerosene, can be marked with red ink. The marks may either indicate the portions to be rejected or may be put at

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[1] In "The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 142.

[2] A regular feature of thermoelectric work of precision. Described in the first paper of this series, Walter P. White, "Thermoelement Installation, Especially for Calorimetry," THIS JOURNAL, 36, 1859 (1914).

regular intervals of a meter or two, corresponding to a note-book record of electromotive force readings. The wire should be supported so that no length greater than a foot or so hangs free in the air, for such lengths, swinging in the earth's magnetic field, cause annoying parasitic currents, which delay the observations. Normally the operation is very rapid. Wire enough for a 24-couple element can be carefully done by two persons, one to observe, and one to run the wire, in less than an hour.

Copper wires
to galvanometer
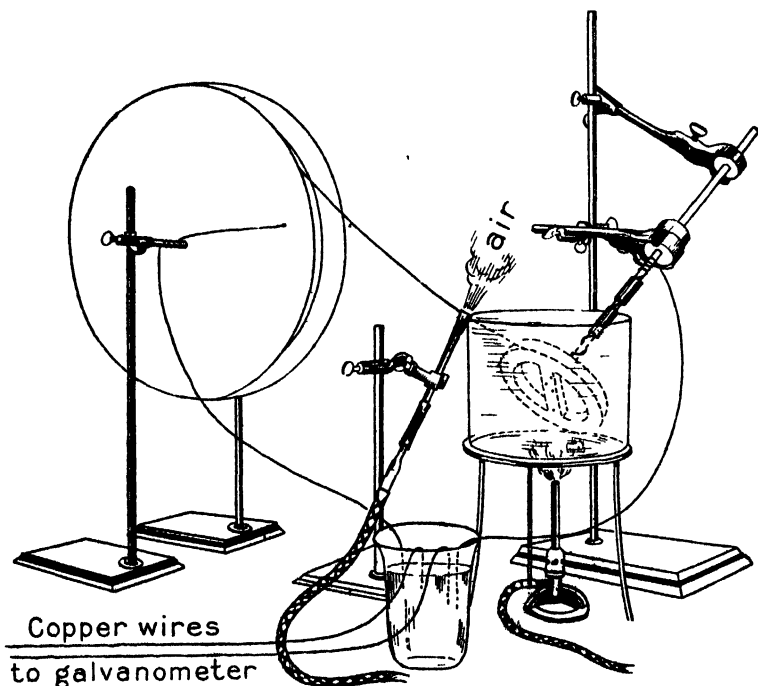
Fig. 3.—Apparatus for testing the quality of thermoelement wire.

Fig. 3 shows one of our wire testers. The drums are both of pasteboard, the axles are wooden dowel rods, the bearings of the inclined axle of the drum in the warm bath are corks, clamped to a retort stand.

6. Making Up the Thermoelement.—After the wire is tested, 2 different methods are possible for selecting the portions to go in the thermoelement. The simplest is merely to cut out the bad pieces of wire (or else put them where they will do no harm)[1] using the rest without further selection. The other method is useful whenever a continuous piece of wire

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[1] Even a very bad portion of wire will do no harm if it is 5 cm. below the level of the bath at either end of the thermoelement.

is available with very few bad spots, and long enough to make the whole, or at any rate half, of the thermoelement. It permits picking out, with certainty, the very best portions of the thermoelement to go in the gradient regions. It is accomplished by winding the wire into a ring, of circumference equal to the length of the finished thermoelement, and then shifting the ring, while partly immersed in a warmed bath, until the most homogeneous portions of the bundle are found.

To accomplish this operation effectively requires a little systematizing. Fig. 4 will give an idea of our present method. The wire is wound on a pasteboard ring, on which a scale of centimeters is marked with red pencil. A light metal rod is clamped to the ring by means of two clothespins, and turns in a bearing (which is merely twisted wire) just at the level of the fluid, thus as the ring is swung up and down, the gradient
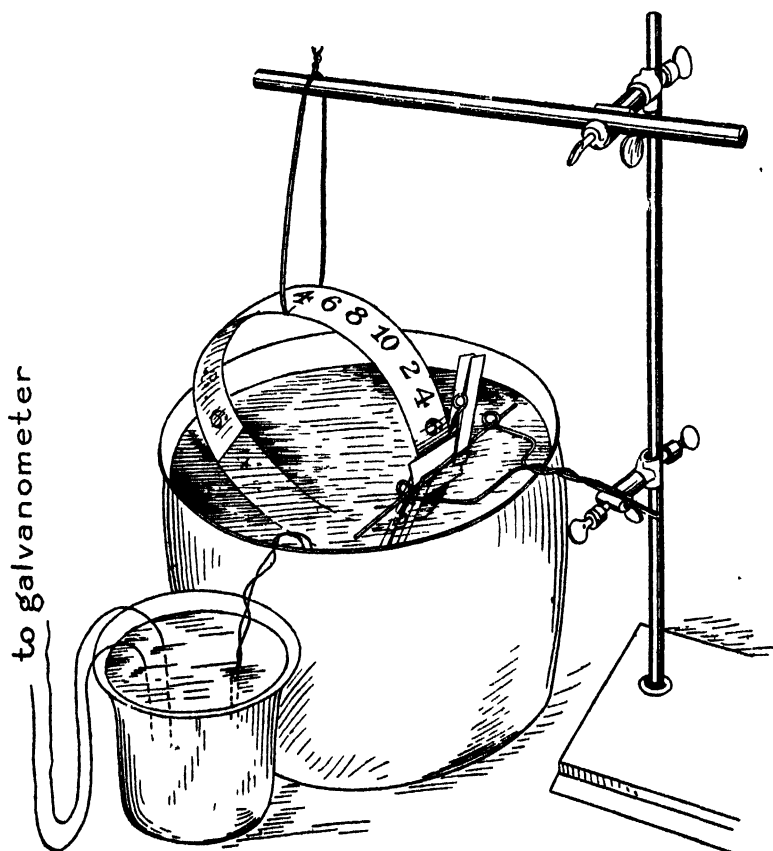
Fig. 4.—Apparatus for locating the best parts of a thermoelement before the wire is cut.

near this rod remains fixed, and the variations in the wire at the other gradient are directly measured. Two plates of sheet copper or aluminum, a few centimeters wide, clamped on with the rod, and projecting a centimeter or two above the liquid surface, will make the fixed gradient still more constant. A blast of air directed against the wires just above the movable gradient will render that gradient sharper and more quickly established after each change. At least two positions of the fixed gradient (and therefore of the rod) will be needed to cover the whole circumference. The leads should be of the same continuous wire, running to copper galvanometer leads as described above for the wire tester. The point where they leave the ring should be always either in the air or in the liquid for any one position of the fixed gradient. The observations obtained by the method just described are plotted against length, the best available portions of the ring are selected for the gradients of the finished thermo-element, and the wires are then cut accordingly. Before the cuts are made a narrow streak is drawn with white paint somewhere across the wires. It is then possible afterward, by bringing the white spots on the wires opposite each other, to be sure that the wires are in the same relative positions as during the test.

III. Construction.

1. Soldering.—In joining up an element, as in testing the wire, it is well to arrange systematically for handling, without confusion, the large amount of small wire. Our wires, therefore, after being cut, are clamped on light boards a decimeter shorter than the element, and with a width of 1 cm. for each pair of junctions. The clamps are little battens of wood, screwed on. Once in place, the wires remain clamped till they are gathered together under loosened battens for inclosure in their case. By this procedure not only is the work made easier and more orderly, but the wire is protected from mechanical strains which might impair its original homogeneity.

A compact and smooth joint is of great assistance in the subsequent operations. This is promoted if the silk insulation is cemented in place by shellac before the wire is cut. Then when the tip of the wire is scraped bare in preparation for being soldered, the adjacent silk remains closely adherent. The copper end, being smaller and more flexible, is wound around the constantan, and tweezers are used, so as to avoid contact with the fingers, which may interfere with the soldering of constantan when rosin is used. A very quick and satisfactory way to do the soldering[1] is by dipping, for the shortest possible time, in a bath of rather hot solder[2] and then snipping off the tip of the junction, thus getting rid of any projecting ends of wire or tails of solder. The exposed portion of bare wire should then be very short; not over a millimeter between the end and the place where perfect insulation begins.[3]

[1] Compare "The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 143.

[2] Rosin is preferably used as a flux, and the rosin is apt, when melted, to loosen the end of the silk. Mr. C. W. H. Ellis, of this laboratory, has used a method which avoids this trouble. The wire, after dipping in melted rosin, is touched with a hot piece of porous fireclay, or other refractory material, which absorbs the excess of rosin, leaving just about enough to do the soldering nicely.

[3] This, of course, involves bringing the solder within half a millimeter or less

2. Insulation.—With the errors from inhomogeneity of the thermo-element made negligible, defective insulation is the only remaining source of error. It is also easily avoided. Some resistance thermometers are provided with special drying material, but the very sensitive inclosed thermo-element seems amply protected against water vapor by a paraffin seal at the point where the leads leave the case.[1] This has been true of thermo-elements used for several years in ice baths, and in one instance, where liquid water had entered through a small hole in a defective case, the thermoelement had recovered its insulation after lying on the shelf a few months with the case still on.

We have never observed any electrical leakage in uninclosed thermo-elements, though slight leakage is not altogether improbable in damp weather if the wires are not well paraffined, just as it might be in any other wires similarly situated.

The junctions, where the silk insulation has been removed for solder-ing, of course need special treatment. The most obvious way is to in-sulate by some kind of varnish,[2] and then simply bunch the junctions to-gether in inclosing.

An easier and more effective method is to distribute the junctions along the tube, letting the inner wires come the farthest, so that the whole group forms a sort of cone with the junctions all on the outside, next the case, which is drawn to a similar cone if glass is used. This method saves the labor of reinsulating, is especially free from liability to failure and gives a thermoelement tip of minimum size and lag. The increase in re-quired depth of immersion which it involves is usually not in the least detrimental.[3]

of the silk without charring that. This is not difficult, with proper attention to the temperature of the solder and the time of immersion. A little preliminary practice is, of course, useful. If the solder is too cold the junction comes out rough. If the end of the silk insulation does become a little loosened, of course no great harm is done, but projecting bits of solder or wire may give considerable trouble.

[1] The thermoelement wires may, without any detriment to the readings, be paraffined throughout their length, and our thermoelements always have been so treated. This may have contributed toward the immunity from dampness which we have observed. At any rate the paraffining seems desirable, in general, for the present, as a precautionary measure. It is best done after the wires are fixed in the case.

[2] Cellulose acetate is apparently the best varnish yet tried. One sample of this gave, after staying a few years in a box, exposed to the atmospheric humidity, a strong smell of acetic acid, and became nearly insoluble in the usual solvent, thus giving strong indications of decomposition. But an 8-junction element, insulated with ma-terial from this same sample, now shows, after two years' inclosure embedded in paraffin, an insulation resistance of over 2000 megohms between the two groups of wires.

A fairly thick coating of varnish is needed, since the varnish tends to gather in the depressions of the surface, leaving the projections (for instance, the outer surface of the copper wires, if these are wound round the others) insufficiently protected.

[3] Four mm. per junction for 24 junctions is unnecessarily open, yet it requires

In cases where the junctions are too numerous to be distributed satis-factorily, or wherever any number of junctions are to be imbedded in metal, reinsulation is of course necessary. A superior method of rein-sulating has recently been introduced by Mr. L. H. Adams, of this labora-tory, who has kindly allowed me to quote his as yet unpublished description of it here:

" * * * The junctions are coated with an insulating layer of vulcanized rubber by the following procedure: Each junction is dipped separately into a fairly thick rubber solution consisting of pure gum rubber dissolved in a mixture of benzene and carbon disulfide. After standing an hour or so, or until dry, the coating of rubber is vulcanized by immersing, for a few seconds only, in a dilute solution of sulfur di-chloride in carbon disulfide (1 to 40). If a thicker coating is desired the operation of dipping in the rubber solution and drying may be repeated several times before the vulcanization. A final drying for several hours at 40° or 50° completes the operation. The coating thus obtained is tough and elastic, and of about the hardness of ordinary sheet rubber. Where, for any reason, a much harder coat of rubber is desired, the fol-lowing method may be substituted: Dip the junctions in a rubber solu-tion in which sulfur is directly incorporated, dry as above and heat to 130–150° for an hour or so.[1] The solution is prepared by adding to the plain rubber solution an amount of precipitated sulfur equal to about 20% of the amount of rubber present.

"Either of these methods gives a tough, coherent and elastic coating of high electrical resistance. In fact, the mechanical and electrical proper-ties even of the softer coating are so satisfactory that the junctions may be imbedded in fusible (Wood's) metal."[2]

3. Inclosure.—The ends of nearly all thermoelements must be enclosed, to allow immersion in baths, etc. A frequent weakness in the case of single or auxiliary elements is to have the inclosing tube stop just above the surface of the bath. The bending of the wire is greatest at the end of the tube, and this bending, and the consequent inhomogeneity intro-duced into the element, thus come in the temperature gradient, where they

a less total depth of immersion than is demanded by many of the best calorimetric resistance thermometers. Twenty-four junctions have been successfully distributed within 2.8 cm., though this degree of concentration is nearly always unnecessary and is undesirable. The distributing can be done more freely if the copper wires are cut a few centimeters longer than the others, otherwise it is necessary to pay attention to the order in which the wires are connected.

[1] Care should be taken that this heating does not injure cotton or silk insulation.

[2] Indications of the production of copper chloride have been observed, Mr. Adams tells me, after treatment with the sulfur chloride. Thorough drying and prompt in-closure of the junctions are therefore desirable, and until more experience has been had, the hard rubber insulation appears safer.

do the maximum amount of harm.[1] The rigid inclosure should come well beyond the gradient into the region of uniform temperature. The middle of the thermoelement may then, in most cases, be left free and flexible. (A slightly flexible prolongation of the rigid tube may advantageously be added to diminish the amount of sharp bending.) With the sensitive multiple elements needed for calorimeter temperatures a complete rigid inclosure will probably be preferred in most cases.

The three main desiderata of a thermoelement end are: small heat capacity, small lag—these are luxuries rather than necessities—and negligible effect upon the reading due to heat conduction along the element from the air above the bath—this is, of course, essential. These three things are all dependent on compactness, and it is the combining of compactness with effective insulation that causes whatever difficulty there is. This difficulty occurs only at the soldered ends, where the original silk insulation has to be removed.

Three kinds of enclosure have been used, glass tubes, metal tubes, and flat metal cases.

Of these the glass inclosure is the easiest to employ, and gives the greatest security against danger of leakage, either of electricity or water. It is therefore preferable in most cases. It is readily made from ordinary soft tubing, fitting the thermoelement rather tight at the ends, and larger at the bends, around which the wires must be pushed into place.[2]

Ordinarily, both ends of a calorimetric thermoelement will turn downward, for insertion in some sort of bath, so that the whole will have much the form of Fig. 5. This figure shows more particularly a glass inclosure, which will usually consist of two L-shaped tubes. The tubes are conveniently held together by a little trough of sheet metal, into which they are either cemented with sealing wax, or clamped. The trough may be made to come at any desired part of the
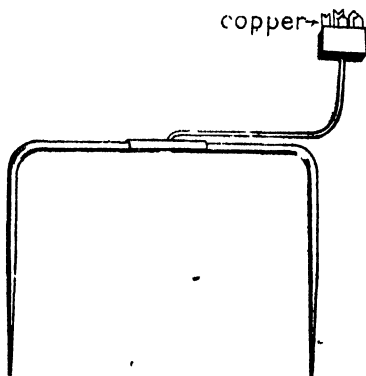
Fig. 5.—A glass inclosed thermoelement.

[1] Compare the section on "General Law of the Inhomogeneous Thermoelement," II, 1, above.

[2] In *metal tubes* the bend is made after the wires are in, and have been tested for insulation, etc. The junctions, whether reinsulated or not, are protected from the tube by a wrapping of silk cloth. This inclosure becomes more desirable as the junctions become fewer, and the need for strength, greater.

With the *flat metal case* the idea is to diminish the lag by making the tube thin, and facilitate insulation by making it wide The uninsulated junctions, staggered to

horizontal portion, and may be used to assist in making thermal contact with a jacket.

In every inclosure the lag is diminished if the junctions are imbedded in paraffin. A fluid (xylol) was about equally effective. Naphthalin gave about half the lag of paraffin, and is therefore generally to be preferred in cases where a reduction of the lag is at all desirable. Otherwise, the paraffin is preferable, on account of its lower melting point and less volatility. Some idea of the effectiveness of different methods can be gained from Table I.

TABLE I.—THERMOELEMENT CONSTANTS.

The length in all cases was 50 cm. The *copper* wires were 0.15 mm. diameter (No. 35).

Diameter of constantan				
wires................	0 26 mm. (No. 30)	0.47 mm. (No. 25)	0.47	0.26
Number of junctions	8	12	24	24
Total resistance.........	42	21	42	126
Diameter of element alone..........	2.6 mm.	4.2 mm	5 2 mm.	.
Diameter of glass tube inclosure............ ...		5.8 mm.	7.0 mm.	5 9
Diameter of metal (brass) tube inclosure.........	3.3 mm.			
Lag, flat metal case, paraffin filling.............	0.9 sec.			
Lag, metal tube, paraffin filling........	3 sec.			
Lag, glass tube, paraffin filling...............		9 sec.	12 sec.	
Lag, glass tube, naphthalin filling...		5 sec.	7 sec.	5 sec.
Sensitiveness, microvolts per millidegree........	0.3	0.5	1.0	1 0
Smallest temperature actually read.........	0.0003°	0.0002°	0 0001°	0 0001°
Water equivalent, 9 cm. immersion....	0.8 g.		1 7 g.	

The required depth of immersion was investigated by putting both ends of the element in a stirred bath at room temperature, with one end passing through a cup containing ice, just above the water. This method is convenient, but exaggerates the effect of conduction, especially for the smaller elements. With the thicker 24-junction glass inclosed element an immersion of 5.5 cm. (average—the uppermost junction was only

keep them apart, are cemented in one or two layers on mica strips, which are thrust into the previously made and tested end cases; the middle portions of the case, including the bends, are then soldered together around the wire. Of the three, this type of inclosure is the most troublesome and most liable to leakage of water, but has a lag and a required depth of immersion which are very low in proportion to the number of junctions.

4 cm. under) reduced the effect of heat conduction on the reading to less than 1/50,000 of the temperature difference between bath and ice.

With the 8 junctions in 3.3 mm. brass tube an immersion of 4 cm. reduced the effect of the ice to 1/4,000 the temperature difference.

4. Curvature of the Bend.—The two bends in the thermoelement of Fig. 5 will often be conveniently located just above the calorimeters, and hence in the temperature gradients. The bends must therefore not be so sharp as to materially affect the thermoelectric power of the wire by the strains produced. Just how sharp they may be without detriment has not been determined, and information on this point would be very welcome, but we have found no perceptible effect from a curve with a radius of 2.5 cm. in No. 30 wire (0.25 mm. diameter), so that this degree of curvature, at any rate, may be considered safe.

5. Terminals.—A precision thermoelement should, by all means, be divided into two equal parts, which can be connected in opposition This gives a ready check upon temporary or permanent defects or changes in the element itself, upon defects of insulation during the construction, and upon the presence of parasitic electromotive forces in the leads outside the zero adjusting switch at the potentiometer. A convenient arrangement of terminals for this purpose, applicable also when the two halves are in separate cases, is shown in Fig. 6. When A^+ and B^+ are the terminals, with B^- and the second

Fig. 6.—Diagram of the arrangement of thermoelement terminals.

A^- joined, the two halves A and B are in opposition; the series arrangement has A^+ and B^- as terminals, with B^+ connected to the first A^-. The arrangement lends itself well to the use of leaves of copper as terminals, which is probably the scheme best combining simplicity with great freedom from thermal forces.

It is well also to add another terminal so connected that 4 or 8 junctions can be read when desirable.

In our own work the thermoelement is checked up, by reversal, at the beginning and end of each day. The operation, which takes less than a minute, gives a guarantee of the integrity of the thermoelement and its insulation, and of the auxiliary switches as well. The divided thermoelement is also an ever ready auxiliary for quickly verifying the condition of the potentiometer. For this purpose one or more stationary or steadily changing temperatures are read with the whole element, and also with one-half of it. One reading, plus or minus the difference of the two halves, which is also observed, should be twice the other. Any accidental change or deterioration in the potentiometer coils used would almost certainly be indicated by a failure of this relation. It does not

seem a very convenient method for a complete calibration of the potentiometer.

If the thermoelement is to be wholly within the calorimeter jacket, or if it is to be protected by the sheet copper shield of Section 2b, in either case the terminals are best not mounted directly upon the case. They may be situated as in Fig. 5, on the end of a slender tube, which is brazed to the sheet metal trough and carries the leads, or they may be at the end of a cable, a meter long or more, made by wrapping the leads with tape, inclosing with the leads a stout cord, a little shorter, for mechanical protection.

IV. Calibration and Testing.

A multiple thermoelement can be calibrated easily and with great precision by comparison with another thermoelement. Of course some thermoelement must have first been calibrated by another method, but this is a service appropriate to the national standardizing laboratories.[1]

All thermoelement calibration can be left to these laboratories wherever that seems desirable, but the secondary calibrations are so easy that they may often profitably be done by the individual experimenter. The checking, testing, or comparing of thermoelements also involve the same principles and precautions as the calibrating.

1. The Precision of the Calibration.—The calibration of an electrical thermometer differs from that of mercury thermometers and many other instruments in that the result can be expressed by a simple equation. It follows that in measuring temperature *intervals* the absolute effect of incorrect calibration will diminish with the interval; the proportional error will be the approximately constant magnitude. And hence, in *making* the calibration, where observations may be made at intervals of 5° to 10°, it follows (1) that the errors in electromotive force measurement will be quite negligible; (2) that errors from inhomogeneity and uneven bath temperature, which tend to increase with the temperature, though they may be noticeable, will still usually be negligible.

To illustrate: In comparing a thermoelement with a standard, dis-

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[1] In a recent paper whose authorship I shared ("The Calibration of Copper-constantan Thermoelements," *Phys. Rev.*, **31**, 159 (1910)), it was assumed that thermoelements would usually need to be calibrated independently by their users, and therefore by some relatively disadvantageous method, and the supposed difficulty of independent calibration has elsewhere been accounted a very serious objection to the thermoelement It now seems that whatever justification these views may once have had at any rate exists no longer. The resistance thermometer is unquestionably easier to calibrate independently, yet in spite of this fact the majority of the calorimetric resistance thermometers now in use in this country were calibrated at the Bureau of Standards. There there seems to be no reason why the thermoelement, which both stands transportation and keeps its calibration at least as well, should not be calibrated at a standardizing laboratory.

crepancies of 0.001° at 40° might sometimes be observed. It would generally be highly erroneous to conclude that the error of such a thermoelement would ever be 0.001° in calorimetric work. The error really indicated would be 25 per million, which is 0.0001° for a 4° interval, and correspondingly less for smaller intervals. If, secondly, the discrepancy of 0.001° should occur during the process of calibration, so that observations at (say) 30° and 40° failed to correspond, the calibration would be out by (in this case) one part in 10,000 through the 10 degree interval between 30° and 40°. In most calorimetric determinations, which involve intervals much less than 10°, the actual error due to the incorrect calibration would thus be much less than 0.001°.

In nearly every case, however, even if a discrepancy of 0.001° should be observed, the occurrence of any such discrepancy during calibration would be very improbable. For such discrepancies, when not due to irregularities in the bath temperature, are caused by a shift—usually a considerable shift—in the position of the temperature gradients. Observations, therefore, which are made with an unchanged depth of immersion and an unaltered ice bath are likely to be quite free from appreciable calibration error. The fact that the consistent series of observations may be 0.001°, or 25 per million, higher or lower than another possible set, is of no importance in calibrating for calorimetric work. Discrepancies, then, observed in comparing thermoelements, are of no importance unless they approach 0.001° in magnitude[1] and unless they also occur during constant conditions as to depth of immersion and arrangement of the bath. In such a case either the portion of the thermoelement used for a gradient, or else the comparing bath, is unsatisfactory.

What has just been said applies to the comparing of a thermoelement with any standard. The comparison against another nearly equal thermoelement has three special advantages:

(1) Only one reading, the difference between the two thermoelements, needs to be made with maximum precision. If the two differ by 1%, the actual temperature needs to be read with only about 0.01 the precision of the differential reading.

(2) The most precise reading is of a small magnitude, and is therefore especially easy to secure, as far as the potentiometer system is concerned.

(3) The constancy required in the bath temperature is less than in a comparison of separate thermometers.

2. *The Bath for Comparing Thermoelements.*—The ease and precision with which thermoelements can be compared are much more likely to

[1] This is on the assumption that a final precision of 0.1 permille is desired. For a less precision a greater tolerance is of course possible.

be realized with a suitable bath.[1] A simple but efficient bath has been made from a tall vacuum jacketed bottle of one liter capacity. The heater is four or five turns of No. 25 silk insulated constantan wire, so coiled that after being fed into the mouth of the bottle it expands and lies against the sides. The stirrer with its tube (supported by a retort stand clamp) is the only other thing required. The tube is long and well centered in the bottle, with the propeller at the bottom. The shaft is inclined slightly in the tube, so as to be near its side at the top, thus giving more space for the thermoelements; a partition surrounds the shaft so as to prevent the thermoelements from coming into contact with it, which might cause a false heating. The tube is wrapped with blotting paper, so as to increase the thermal separation between the ascending and descending columns of liquid. (The current should of course be upward in this tube.) It appears probable from our experience, and also from a consideration of the physical actions involved, that the stirring may easily be too vigorous, and that it should never furnish nearly as much heat as the heating coil, for that is equivalent to putting a considerable part of the coil directly in the tube at the bottom—a thing which no one would think of doing. By the use of a few cork pulleys, very easily and quickly made, the speed of stirring is made to vary with the temperature elevation.

3. Tests Preliminary to the Calibration.—(From here on the calibration of one thermoelement against another will be the only case considered, and 24 couples will be assumed.)

Two sources of error are to be considered in calibrating: the discrepancies in reading discussed in Section 1, and the effect of differences in the lag of the two thermoelements. It is well to determine in advance the possible magnitude of these two errors; this may save many unnecessary precautions, and will make more certain the value of the results.

The effect of a difference in lag of course depends on the rate at which the bath temperature is changing. It will probably be simplest not to determine the lag as such, but to find at once the relation of rate to error. If, for instance, a change in bath rate of 20 microvolts per minute (say, a change from +5 to —15 per minute) should produce a change of 0 2 microvolt in the differential reading for the same centigrade temperature, then for any rate under 5 per minute the effect on the differential reading would be less than 0.05 microvolt. The rate can easily and

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[1] In a previous paper a very simple and satisfactory electrically heated comparing bath was described ("The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 147) whose essential features were extreme symmetry and an upper chamber kept a very little hotter than the rest. This bath, which was packed in cotton wool, was rather slow in settling down to a constant temperature. This made its operation rather tedious with elements of large lag, for whose accurate comparison a nearly constant temperature is desirable. Accordingly, the present bath has been substituted.

quickly be made small enough by a little regulation of the bath heating current,[1] and should be measured for each determination.

The discrepancies in thermoelement readings, whether due to inhomogeneity or to uneven bath temperature, will vary as the thermoelements are moved, and especially as they are moved up and down. It is therefore possible to estimate very quickly how great are the discrepancies to be expected during the calibration. In making such estimates, it is probably safe to consider that the effective level of the calibration bath will not vary, as a result of temperature change alone, by more than 1 cm., and the addition of a copper collar around the thermoelement will make the gradient still more constant in position.

If more definite information as to the quality of the thermoelement is desired it can be satisfactorily obtained as follows. The thermoelement is clamped by the middle at such a height that two vacuum-jacketed bottles, full of ice and water, can be moved up and down while they surround the vertical ends. The gradient at either end can thus be shifted up and down without making any other change. By clamping a trough of sheet metal under the horizontal part of the thermoelement, and piling fine ice in this, the gradients can be extended around the bends and along toward the center. In one instance the effect of a shift in the ice level was practically complete in 3 minutes, in a glass-inclosed twenty-four junction thermoelement, when the gradient was moved upward.

4 Conduct of a Calibration —In comparing thermoelements, the simplest way to treat the cold junctions is to put them in an ice bath, and this is quite accurate enough for all ordinary purposes. The bath should be adjusted 15 minutes or so before being used, and should not be stirred or disturbed during a series of observations, except that the ice melting at the top should be replaced, and the level kept as constant as possible.

With the ice bath in use it is necessary to read only (1) the total electromotive force of one of the thermoelements and (2) the difference between their readings, differentially. The total electromotive force readings, made at regular time intervals give the bath rate. As soon as this has been made small enough, the differential reading is taken. This reading and the *corresponding* total electromotive force are the necessary data for that temperature. Since the total E. M. F. observations need be accurate only to 5 microvolts, while the bath rate must usually be less than 5 microvolts per minute, observations taken within a minute of each other will correspond sufficiently, so that the observing of two different electromotive forces presents no difficulty even with very simple potentiometer arrangements. It will save considerable work in the calculations if the data correspond to round numbers of microvolts of the total E. M. F. of the thermoelement undergoing calibration. This

[1] A quick and convenient method, also, is to change the heating current so as to reverse a rather slow rate, and then read during the minute or two of nearly constant temperature which occurs as the rate passes through zero.

does not necessitate bringing the bath within 0.005° of the round value; it is sufficient to observe within 0.1° of it and apply a correction, or interpolate between readings on both sides. The ratio of the differential reading to the total E. M. F. may usually be taken as constant over 0.5°.[1]

5. Getting the Working Table from the Calibration Data.—The E. M. F. of most thermoelements between 0° and 100° can be expressed with high precision by a cubic equation with temperature as the independent variable, and still better by an exponential equation,[2] so that there is no difficulty in getting a complete calibration which has all the precision of the observations and the standards used. This, however, is in practice mainly a question for the standardizing laboratories, since the thermoelement user will want tables in which E. M. F. is the independent variable. No advantageous formula has yet been found for making such tables, so that the best way to get them is probably to apply small corrections to a suitable preexisting table.[3] The best preexisting table to use will generally be one derived for another thermoelement, since the differences are then most likely to follow a simple law.[4]

A good method for making the corrections is in detail as follows: It has been suggested above that the calibration points be, by an easy interpolation or otherwise, found for round values of the E. M. F. of the thermoelement calibrated. The differential readings, added to (or subtracted from) these, give the corresponding values for the standard, from which the true temperatures can of course be found. If, now, the microvolt readings E_1, E_2, . , of the calibrated element, are taken to the preexisting table (which may be the table for the standard), tempera-

[1] This value is calculated on the assumption that the two thermoelements differ by 1%. If the difference is greater or less than this the *safe* limits of an assumed constant ratio will change about in inverse proportion.

This nearly linear ratio may be taken advantage of to obtain a method of calibration in which the ice bath is avoided, and greater certainty thus obtained The cold junction is put in a gently stirred bath in a vacuum-jacketed bottle, which is kept nearly constant by immersion in a thermostat, or which may be in any bath which never differs from it in temperature by more than 0.2°. A correction for the slight possible temperature variations in the bottle is readily made by using the linear ratio of electromotive force to electromotive force difference over the small intervals involved. The temperature of this bottle is accordingly measured, but with a precision which need not be better than 0.003°.

[2] L. H. Adams, "A Useful Type of Formula for the Interpolation and Representation of Experimental Results," *J. Wash. Acad. Sci.*, **3**, 469 (1913).

[3] R. B. Sosman, "The Platinum-Rhodium Thermoelement from 0° to 1755°," *Am. J. Sci.*, [4] **30**, 1 (1910); see also L. H. Adams, "Calibration Tables for Copper-Constantan and Platinum-Platinrhodium Thermoelements," THIS JOURNAL, **36**, 72 (1914). The present method, however, is in detail somewhat different from that of Sosman

[4] Such a table, consistent to 0.00001°, has been derived, and will soon be placed at the disposal of the users of thermoelements.

ture readings Θ_1, Θ_2, ... will be obtained, which are not the true temperatures, since the table was not made for the *calibrated* element; but the differences between these and the true temperatures Θ_1', Θ_2', ..., added to the numbers in the table, will evidently give tabular values which *are* true for the calibrated element. This gives values for the temperatures taken in the calibration. To get values for other temperatures, parabolas are derived, giving the differences $\Theta_1' - \Theta_1$, $\Theta_2' - \Theta_2$, ... , in terms of the E. M. F.'s, E_1, E_2, ..., and from these parabolas other values of $\Theta' - \Theta$ are obtained. Since these values are derived from a smooth curve, any errors in using them will diminish with the interval measured. Experience shows that if the original intervals are $10°$ the maximum error introduced by assuming the absolute correctness of a parabola will not exceed $0.0002°$ in $5°$, which is a little larger than the probable proportional error due to the calibration, but further experience may very likely reduce this limit. If the original observations are at intervals of $5°$, the error in the parabolas is quite negligible. Hence a five-degree interval must, for the present, be considered the best in calibration, unless the two thermoelements differ by less than 3 per mille, when a ten-degree interval is quite sufficient.

In calculating thermoelement tables the calculations should be carried out to a precision somewhat greater than is to be used in reading the thermoelement, even if this precision is considerably better than was reached in the calibration observations, because the error due to the calibration observations will decrease with the interval measured, so that for small intervals the needless errors due to insufficient carrying out of the reckoning might be the largest present, unless these are made less than the error of reading.

6. Working Tables.—With a 24-couple copper-constantan thermoelement it is possible to have a calibration table which though short (and therefore easily constructed), yet gives a very easy interpolation. This possibility arises, first because the ratio of E. M. F. to temperature is nearly constant, and second, because the unit of measurement, the microvolt, corresponds very closely to a decimal submultiple of a degree, namely a thousandth.[1] This is illustrated in Tables II and III. Table II is a small portion of a table of an actual thermoelement, arranged with 100-microvolt intervals, that is, with only 10 steps per degree. Table III is the same, written so as to give the number of millidegrees which must be added to the number of microvolts in order to give the true temperature. Here the difference is only about $0.0027°$, so that the interpolation is easy. (The ease of interpolation can also be readily secured in using Table II, but is more apparent in Table III.)

[1] The possibility, therefore, may occur with the resistance thermometer, since this may be made to have the same two properties.

TABLE II.		TABLE III.		TABLE II.		TABLE III.	
Microvolts.	Degrees.	Millidegrees minus microvolts.	Diff.	Microvolts.	Degrees.	Millidegrees minus microvolts.	Diff.
8000	8.29720	297.2		8500	8.81082	310.82	
			2.78				2.65
100	8.39998	299.98		600	8.91347	313.47	
			2.73				2.62
200	8.50271	302.71		700	9.01609	316.09	
			2.73				2.61
300	8.60544	385.44		800	9.11870	318.70	
			2.70				2.59
400	8.70814	308.14		900	9 22129	321.29	
			2.68				2.57
8500	8.81082	310.82		9000	9.32386	323.86	

7. *Measurement of Intervals.*—The ease and precision of the whole system of calorimetric measurements described in the present series of papers depend, to a considerable extent, on the fact that changes of temperature, not temperatures, are the subjects of the more accurate observations. The cold junction temperature, therefore, if constant, need not be known with high precision, for it is added both to the initial and to the final reading of the calorimeter thermoelement, and its errors disappear in the resulting subtraction.[1] The ratio of microvolts to degrees, however, in copper-constantan, changes about 0.002 per degree, hence on this account the cold junction temperature must be known to 0.05° for a precision of 0.0001, and correspondingly for other degrees of precision. This requirement is easily met—by means of a moderately good mercury thermometer, for instance. If the cold junction temperature is measured in degrees, it must, of course, be reduced to microvolts before being added to the thermoelement readings. This reduction needs to be correct only to 50 microvolts or so.

Summary.

Inhomogeneity, once a serious foe to precision in thermoelements, and still often supposed to be such, can, without difficulty, be rendered practically negligible in copper-constantan thermoelements used for any precision up to 50 parts per million. Such thermoelements, accordingly, may, except for imperfect insulation, easily preventable, be free from all appreciable errors other than those (such as incomplete depth of immersion) which are possible with all thermometers. To attain this freedom from error the wire used must be tested, and the essential though easily satisfied requirements peculiar to a thermoelectric system must be observed. These this paper attempts to consider in detail, and it also describes simple but important details regarding the operations of construction, insulation, inclosure, calibration, etc., of the thermoelements.

[1] One feature of the system is a provision for eliminating the effect of *change* in the cold junction temperature; this is treated in a subsequent paper.

Constantan wire for thermoelements has been so far improved that continuous lengths are frequently obtainable which vary (in electromotive force against copper) less than 0.0002, making sensitive thermoelements with errors usually less than 20 per million.

The testing of wire enough for a thermoelement of maximum sensitiveness takes but an hour or two, with simple apparatus.

On account of the ease with which thermoelements can be constructed, the more sensitive combination of several couples is generally preferable to a single couple, even for cruder measurements.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D C

EASY CALORIMETRIC METHODS OF HIGH PRECISION.

BY WALTER P WHITE
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In calorimetry by the "Method of Mixtures" a precision of 1 per mille appears to be generally counted excellent. It scarcely deserves, however, to be considered high at the present time. Calorimetric precision depends more on the adequacy of the apparatus than on any special skill exercised by the observer, and it has been found that appropriate apparatus and methods are easily attainable which will yield a precision approaching 0 1 per mille with little more labor than is needed to get 1 per mille with some customary arrangements.[1] It is true that 1 per mille appears in most cases to be quite sufficient. Errors in associated temperatures or defects in chemical purity are often such that a higher calorimetric precision would be of comparatively little value. Nevertheless, there are cases where a higher precision is desired, and these will doubtless increase with the general progress of science; often, too, the associated measurements or the chemical purity attained have probably really been governed by the limitations of the calorimeter, and would readily be improved if greater calorimetric precision should appear less difficult to get; finally, there are many determinations where, though high relative precision may not be desired, yet high absolute precision is necessary on account of an unavoidable small temperature interval (in measuring heats of dilution, for instance). A relative precision of from 1 to 0.1 per mille, and an absolute precision of from 0 001° to 0 0001° are therefore of interest, and these are in view in the present paper.

Precision in calorimetry depends first upon the temperature measurement, and second upon the determination of the heat which escapes and is determined indirectly. The control of the heat losses has been made not only sufficient for the highest precision but convenient, owing mainly

[1] One-fiftieth per mille has been reached, under specially favorable conditions.

to the introduction of convenient and simple arrangements for complete inclosure of the calorimeter by the jacket. With this complete inclosure given, the other essentials of effective control, namely, accurate measurement of the jacket temperature and control of evaporation and heat of stirring, are easily added. In the temperature measurement electric thermometers give high precision, but their relative convenience is not so evident. This convenience, however, has been increased in the case of the resistance thermometer by the work of recent years, and especially by the improvements of Dickinson and Mueller, who have produced instruments convenient enough for commercial work, and also capable of more than commercial precision under proper conditions. .

The differential thermoelement is inherently free from the most serious sources of error affecting the resistance thermometer, and hence affords methods which, on account of the extraordinarily few precautions needed in them, are highly convenient as well as certain. The electrical arrangements and their advantages have been described in detail in previous papers of the present series.[1] Some of these advantages are obtained at the expense of a slight complication on the calorimetric side. The present paper deals with various arrangements by which this disadvantage can be minimized.

The complication is the addition of a second calorimeter, the comparison or "cold" calorimeter, in place of the more familiar ice bath around the "cold" end of the thermoelement. The advantages thereby secured are, first, avoiding the ice bath and its small errors, and second, gaining the power to make the measured temperature difference as small as the change in the working calorimeter, and hence securing a precision which, up to a certain point, becomes greater as the measurement becomes more delicate, and thus tends to increase in proportion to the need for it. The exact temperatures of the two calorimeters are of no importance. The changes in the temperature of the added, or comparison, calorimeter are determined along with those unavoidable in the working calorimeter, and therefore add practically nothing either to the error or to the number of observations required.

One method of this sort has already been employed,[2] especially in Germany, with the second calorimeter an exact duplicate of the first. The differences, however, between that earlier method and those here described are rather important. First, the thermoelements and the auxiliary ap-

[1] "Thermoelement Installation, Especially for Calorimetry," THIS JOURNAL, 36, 1856 (1914); "Potentiometers for Thermoelectric Work, Especially in Calorimetry," Ibid., 36, 1868; "Leakage Prevention by Shielding, Especially in Potentiometer Systems," Ibid., 36, 2011; "Thermoelements of Precision," Ibid., 36, 2292.

[2] H. von Steinwehr, Z. physik. Chem., 38, 185 (1901); H. Hausrath, Ann. Physik, 9, 522 (1902); G. Rümelin, Diss. Gött., 1905; Z. Physik. Chem., 58, 449 (1907); H. Magnus, Ann. Physik, 31, 597 (1910); Z. Instrumentenkunde, 32, 127 (1912)

paratus of the German investigators were less developed; and therefore, while admirably adapted to their object, the securing of great delicacy with a very simple installation, they were not very flexible nor favorable to high relative precision. Second, the German investigators attached far greater importance to the strictly calorimetric advantages of the twin calorimeters—that is, to the partial compensation of heat losses which resulted from the similarity of the two. In the present methods a still better control of heat losses had already been attained by thorough jacketing; the second calorimeter thus became of value solely as an aid in temperature measurement, and arrangements more accurate and much more convenient than the twin became possible.

The validity of our methods of treating the second or "cold" calorimeter can perhaps be most directly shown by means of the very simple mathematical analysis of the thermal actions involved, which at the outset convinced us of the relative inferiority of the twin arrangement. This analysis is the more worth while since the notion is very plausible, and is probably widely held, that similarity in a pair of calorimeters, by providing an automatic compensation of certain thermal actions, is able to remove serious sources of error.

1. Thermal Relations of the Calorimeters.

Consider two calorimeters, or other bodies, the active one a, and the blank, or comparison body b. Let

Θ_a, Θ_b be their temperatures.

C_a, C_b the temperature of the chamber (jacket) in which each is;

K_a, K_b their cooling factors, as dependent on the chamber, that is, as defined by ($e.\ g.$),

$$d\Theta_a/dt = (C_a - \Theta_a)K_a$$

k_a, k_b their cooling factors toward each other, defined by ($e.\ g.$),

$$d\Theta_a/dt = (\Theta_b - \Theta_a)k_a$$

w_a, w_b temperature change due to evaporation and stirring.

$d/dt\ (\Theta_a - \Theta_b)$ is then the rate of change of the differential temperature, that is, of the temperature which is observed with the highest precision and which, when corrected, gives the calorimetric interval.

Then, in the most general case, considering only the heat passing to or from the environment,

$$d/dt\ (\Theta_a - \Theta_b) = K_a(C_a - \Theta_a) - K_b(C_b - \Theta_b) + \\ k_a(\Theta_b - \Theta_a) + k_b(\Theta_b - \Theta_a) + w_a - w_b. \quad (1)$$

If the bodies are in the same jacket, this becomes

$$d/dt\ (\Theta_a - \Theta_b) = K_a(C - \Theta_a) - K_b(C - \Theta_b) + \\ (k_a + k_b)(\Theta_b - \Theta_a) + w_a - w_b, \quad (2)$$

which may also be written:

$$d/dt\,(\Theta_a - \Theta_b) = (K_a + k_a + k_b)(\Theta_b - \Theta_a) +$$
$$(K_a - K_b)(C - \Theta_b) + w_a - w_b. \quad (3)$$

If the calorimeters can be treated as equal the last two terms vanish, and we have the very simple expression:

$$d/dt\,(\Theta_a - \Theta_b) = (K + 2k)(\Theta_b - \Theta_a) \quad (4)$$

Equations 1, 3 and 4 are, of course, the formulae for finding the cooling corrections under the different conditions described.

2. The Twin Calorimeter Method.

From these equations the limitations of the twin calorimeter methods are easily seen. Equation 4, to be sure, is exceedingly simple, and the external temperature does not appear in it at all, so that complete independence of the environment and its changes appears to have been gained. But Equation 4 applies only to the ideal case of the twin method, the case where the calorimeters are identical twins in a perfectly uniform environment. In practise, there will be differences in the cooling rates K_a and K_b, and irregularities in the exterior temperature distribution, so that (3) or even (1) will be the correct equation. But these equations are not practically usable, and yet a neglect of the extra terms they contain can easily be shown to involve a danger of error. For instance, if K_a and K_b differ by only 5%, and external temperatures are so uniform that (3) holds, then $C - \Theta_b$, the temperature difference of jacket and cold calorimeter, must ordinarily be *and remain* less than the change in the working calorimeter, in order that (4) may be used without an error of 1 per mille, and less than 0.1 of that change for a precision of 0.1 per mille.

There are three methods of diminishing this difficulty, but, even so, the twin arrangement remains less advantageous than that described below. These three methods are:

(1) By a very careful adjustment of the equality of the calorimeters and of the uniformity of their immediate environment. This is, in general, decidedly troublesome.

(2) By running a "fore" and an "after" cooling period, as in the Pfaundler method with single calorimeters. The errors from the extra terms in (1) and (3) are then considerably diminished, as can easily be shown. This requires 3 observation periods, and is thus more laborious than the other methods given later (which require but 2) besides being less accurate.[1]

(3) By using a completely-inclosing jacket, so that the total effective temperature around the calorimeters can be definitely known, and then taking advantage of this knowledge to make $C - \Theta_b$, the jacket-cold-

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[1] It is, however, more accurate than the same three-period method with a single calorimeter.

calorimeter temperature difference of Equation 3, negligibly small, so that the term containing it vanishes and Equation 4 *practically* applies.[1] Since approximate temperature adjustments are easily made, and since a very rough approximation to equality between the two cooling rates, K_a and K_b, is now sufficient, this method is not laborious. The working calorimeter alone, however, is now quite as effective as the twin arrangement, since (1) the jacket-calorimeter temperature difference, which must be measured to get the cooling correction of the single calorimeter, is numerically almost the same as the temperature difference between the two calorimeters, which plays a corresponding part in work with them, and (2) the effect of irregularities in the jacket temperature is similar and rather larger with the twin arrangement.[2]

The duplicate calorimeter, then, is as a rule of no advantage thermally

[1] The German investigators who have worked with the twin calorimeters have, in general, used the first two of these methods, and also got some of the benefits of the third by initially adjusting to equality the four temperatures of the room, of the (incomplete) jacket, and of the two calorimeters. Their methods were thus effective but laborious, and need not be further treated here. Two special features of their procedure, however, appear to deserve comment, since they have to do with principles of general application in calorimetry.

One of these features occurs in A. Magnus' very interesting and ingenious installation (*Loc. cit.*). Magnus used calorimeters holding 60 liters, and did so for the purpose of diminishing the cooling correction. If his intention was to increase also the quantity of heat measured, keeping the temperature interval the same, the procedure was correct. In comparison with calorimeters of one twenty-seventh the size, or 2.2 liters, the heat losses would be only one-third as great, since the surface, though nine times as great, is smaller in proportion to the amount of heat measured. If, however, the intention was to measure the same amount of heat with the larger calorimeters, the ninefold surface would mean a ninefold increase in the effect of irregularities and uncertainties in the external temperature, to which in most installations (including, probably, that of Magnus) nearly all the heat loss errors are due. In such a case, then, these errors not only fail to be decreased, but are largely increased by the use of such Gargantuan calorimeters.

Another notable feature of some previous work is the use of insulating layers, as of cork, between the twin calorimeters. As to that, all methods based on (3) or (4) have one advantage which deserves mention. The direct heat flow from one calorimeter to the other (terms containing small k_a and k_b) does not complicate the case at all, not even if K_a and K_b are unequal, as is evident from (3) and (4). To bring the jacket in between, so as to prevent a direct heat flow, is a superfluous complication; to put between any heat insulating material (as has often been done) is an unmitigated disadvantage, since any such layer will have a lagging temperature, and its insertion therefore means the introduction of a real error in order to avoid a purely imaginary one.

[2] The jacket temperature is more changeable than that of the cold calorimeter, and hence might need to be measured more frequently; but this fact is of no practical importance in most cases, especially since the working calorimeter temperature is usually more changeable than that of the jacket, so that it governs the number of observations needed.

when a complete jacket is used, and is comparatively unsatisfactory whenever a complete jacket is not used. Its real advantage, therefore, is not calorimetric but thermometric; its usefulness lies almost entirely in securing the simplicity and the high precision of the differential thermo-electric measurement.

3. The Compensated Cold Calorimeter.

Two features distinguish our present method, the "Compensated Calorimeter Method." First, the second calorimeter is simply a vacuum-jacketed vessel, whose cooling factor (lag constant) is from one-fifth to one-tenth as great as that of most duplicate calorimeters would be. Thereby all adjustments of the temperature of the second calorimeter, or of the amount of water in it, as well as all temperature measurements or distributions affecting it, need but one-fifth, or less, of the precision needed in a twin installation. Indeed, as we shall see presently, the use of such a vessel as cold calorimeter reduces to one-fifth, or less, the precision needed in adjustments affecting the cooling constant of the working calorimeter also. This arrangement, considering the heat losses alone, is still not quite so good as a properly jacketed single calorimeter, but its errors are a little less, and its convenience much greater, than with the twin method.

The second feature is a specially arranged thermoelement combination, used for the cooling correction determination, and made necessary by the fact that Equation 4 does not apply unless the cooling corrections of the two calorimeters are equal. The combination consists of two auxiliary thermoelements, each running from the jacket to one of the calorimeters. These thermoelements are connected in series, so that their combined E. M. F. is obtained by a single reading. One of the thermoelements is compensated for the difference in the cooling constants of the calorimeters, that is, it is adjusted so that its sensitiveness is to that of the other thermoelement in the same ratio as the cooling constants of the respective calorimeters. Each reading will then be proportional to the temperature rate of its particular calorimeter, and the combined reading to the resultant change in both. For instance, one of our comparison calorimeters has a cooling factor which is one-sixth that of the working calorimeter, and its auxiliary thermoelement is accordingly made one-sixth as sensitive as that of the other. A given electromotive force in this auxiliary, therefore, accompanies six times as large a temperature interval as with the working calorimeter auxiliary. But this six-fold temperature difference, acting upon the six times smaller cooling factor, produces the same rate of temperature change, and therefore the same magnitude of effect on the main differential thermoelement, as would accompany the same electromotive force in the working calorimeter auxiliary. The change in the main thermoelement will therefore be proportional

to the reading of the combined auxiliary elements, whatever their individual electromotive forces may be, and hence that combined reading may be used like $\Theta_b - \Theta_a$ in the *second* member of Equation 3 or 4, giving a cooling correction formula as simple as that of the twin arrangement, or as that of a completely jacketed single calorimeter.[1]

Of course this compensated arrangement demands a complete and uniform jacket. But since such a jacket is easy to make (see Fig. 3 in Section 9b), saves many uncertainties and precautions, and is necessary for very high precision with other methods, this requirement cannot be considered a real drawback.

The lower sensitiveness of the auxiliary thermoelement of the cold calorimeter is obtained, in part, by using fewer couples, but also, as a rule, by the use of a shunt. By providing several interchangeable shunts, several working calorimeters can be used with the same cold calorimeter and auxiliary thermoelement. The adjustment of the shunt demands a determination of K_a and K_b (the two cooling rates) at the time the calorimeters are first put in commission. A very approximate determination suffices, however. This is because K_a, the cooling factor of the working calorimeter, will seldom be strictly constant, hence there is no advantage in maintaining or measuring K_b with great precision; instead, the temperature difference $C - \Theta_b$ of Equation 3 is kept small, as suggested above (Section 2), in order to make negligible the term containing $C - \Theta_b$. For the same reason, the shunt need not be very *constant;* a copper shunt,

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[1] The equation for this arrangement, corresponding to Equation 3, is obtained as follows·

Let n be the ratio of the two cooling rates K_a and K_b. Then the reading of the cold calorimeter auxiliary will be made proportionate to $\dfrac{\Theta_b - C}{n}$. Since Equation 2, omitting the small k's, may be written:

$$d/dt\,(\Theta_a - \Theta_b) = K_a\,(\Theta_a - C) - n\,K_b\,\frac{\Theta_b - C}{n} + w_a - w_b$$

we may have instead of (3):

$$d/dt\,(\Theta_a - \Theta_b) = K_a\left(\Theta_a - C - \frac{\Theta_b - C}{n}\right)$$
$$+ (K_a - nK_b)\,\frac{\Theta_b - C}{n} + w_a - w_b$$
$$= K_a\left(\Theta_a - C - \frac{\Theta_b - C}{n}\right)$$
$$+ \left(\frac{K_a}{n} - K_b\right)(\Theta_b - C) + w_a - w_b \qquad (3a)$$

where $(\Theta_a - C - (\Theta_b - C)/n)$ is the combination auxiliary reading, and $K_a/n - K_b$, like $K_a - K_b$ of (3), is the difference of two nearly equal quantities. In this, the error term, here, K_a appears divided by n—that is, every error due to variation in the cooling rate of the working calorimeter is diminished by reducing the cooling rate of the other.

which may possibly vary nearly 5% as a result of temperature changes, is admissible, though a shunt mainly of manganin, constructed so as to be thermoelectrically neutral, is usually more convenient. The temperature difference of jacket and cold calorimeter, $C - \Theta_b$, can be as large as 0.2°, and a simultaneous variation of 5%, both in K_a and in the resistance of a copper shunt, will not cause an error of 0.0001° in a period of 10 minutes. If K_a is likely to be constant to 2%, as will often be the case, and the shunt is of manganin, adjusted to 2%, $C - \Theta_b$ may vary 0.5°. For longer intervals, of course, the tolerance is correspondingly less.

If the working calorimeter is also a vacuum-jacketed vessel, the cold calorimeter can profitably be made like it, and then there will usually be little to choose in efficiency between the compensated and the twin method.

4. Divided Installations.

All the important advantages of the above method can be secured if the two calorimeters are in separate jackets which are at different temperatures. The only requirement is to let each section of the combined auxiliary thermoelement run to the jacket surrounding its own calorimeter. The two can be as easily connected and read in series as if they ran to the same jacket.

The comparison calorimeter and its jacket must have the same equality of temperature as is necessary with a single jacket, and departure from this brings errors of the same amount;[1] the jacket around the working calorimeter may have any varying value, just as in work with a single calorimeter.

This method is more adaptable than the single jacket method, and is, of course, essential if adiabatic methods are to be used. It is a little more expensive if constructed from the start, but less so where a jacketed single calorimeter is already at hand.

5. Thermostats.

With a single calorimeter it is often convenient to make the jacket a thermostat. This may save considerable tiresome preliminary adjusting of temperatures, renders the subsequent observations more uniform, enables determinations to be more readily compared, since all have the same initial temperatures,[2] and reduces the necessity of dealing with troublesome temperature coefficients in thermochemical work. With a comparison calorimeter still further advantages of the thermostat appear; the equality of temperature between the jacket and the comparison calorimeter may be made more exact with less trouble, and hence greater

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[1] That is, errors depending only on the difference $\left(\dfrac{K_a}{n} - K_b\right)$ of Equation 3a.

[2] The supply of water for the working calorimeter can conveniently be kept in a bottle immersed in the thermostat jacket.

latitude is allowed in the permanent adjustment of the compensating shunt (of the auxiliary thermoelement), and also in the temporary values of the cooling factor of the working calorimeter, all of which makes for ease and precision. With the high precision appropriate to the differ-. ential calorimetric methods, however, there arises a difficulty in using a thermostat with an *ordinary* calorimeter. With such a calorimeter a precision approaching $0.0001°$ usually demands that the differential temperature, in which the jacket enters, be measured to better than $0.003°$. But if the jacket temperature is oscillating through $0.01°$ or so, any one measurement of it may be $0.005°$ from the mean, so that there may be an error of $0.005°$, unless an unusually and objectionably large number of observations is made. The difficulty can be avoided: (*a*) by using a thermostat accurate to $0.001°$, methods of doing which will probably be discussed later on. (*b*) By putting within the thermostat only the vacuum-jacketed calorimeter, whose low cooling factor renders a constancy of $0.01°$ sufficient; foregoing, of course, the advantages of a thermostat around the working calorimeter. (*c*) By working the thermostat with the heater very near the regulator bulb, which makes the oscillations shorter, and therefore smaller; the resulting increased influence of room temperature upon the bath will act too slowly to be troublesome. (*d*) By increasing the lag of the jacket ends of the auxiliary thermoelements, so that the reading depends on the *mean* temperature of the jacket. This can be done by pulling over a rubber tube. There need be no fear for the accuracy of this method, since the only objection to the thermostat is that a single reading of an oscillating temperature is usually not representative.[1]

In a thermostat used as here indicated, if the heater is put near the bottom, there is no need whatever to have the stirrer in operation except during the determinations and for a few minutes before.

If the thermostat is constant to $0.01°$, the cold calorimeter can (ordinarily) be made to have quite negligible temperature fluctuations, and so can be used simply as a body of constant temperature, constituting a frequently advantageous substitute for an ice bath.[2] The addition of the compensated (*i. e.*, shunted) auxiliary thermoelement (not yet devised in 1910) improves this method, so that its original form may be said to have been superseded. Used with the shunted auxiliary, of course, it is nothing but the regular compensated calorimeter method as used with a thermostat.

The copper block formerly suggested for the comparison calorimeter also seems less desirable than the present arrangement. Although such a block has been used (independently) in other laboratories as a *working* calorimeter, as a comparison calorimeter it is less effective, and probably less simple to instal, than a vacuum-jacketed bottle with a simple stirrer.

[1] If the oscillations of the thermostat temperature are too slow, however (a minute or more) they may make a more than negligible unevenness in the variation of the calorimeter temperature

[2] Described from this laboratory in: "Some Calorimetric Methods" (*Phys. Rev.*, **31**, 557 (1910)) under the name of "comparison body."

6. Compensation of the Stirring.

With twin calorimeters the heat of stirring in each is naturally compensated by that in the other, and the same compensation can easily be obtained by a little adjustment, where the two calorimeters are unlike. This is a possibility belonging only to two-calorimeter systems. There will usually be considerable doubt, however, as to whether the compensation is better than the alternative procedure, which is to make the stirring of the working calorimeter so constant that variations in the heat produced are negligible, at the same time simply making the stirring very slow in the cold calorimeter, which will always be admissible. The constant stirring may perhaps call for a governor; the compensation demands that the stirrers of the two calorimeters be somehow geared together, and that with each of them pains be taken to see that no change in conditions is allowed to occur which may affect the relation of heat produced to speed of stirring. Experience of the relative merits of the two procedures appears to be wholly lacking; a brief discussion of calorimeter stirring in general has been published elsewhere [1]

7. Experience with the New Methods.

The "Comparison Body" method, and, subsequently, the "Compensated Calorimeter" method, have been used in the Geophysical Laboratory for the last two years. Their *convenience* has been clearly shown. The work thus far done with them, and the auxiliary apparatus used, have not been adequate to show the *precision* of which they are probably capable, but some indication of it has been obtained in the following case Eight regular calorimetric determinations were extended to occupy an hour, when it was found that for successive ten-minute intervals the temperature observations were concordant to 0 000070° on the average. Even with absolutely perfect apparatus an average variation of 0 000035° would, in accordance with the laws of chance, have resulted from the fact that the record was only made to 0 000100°; the average *error*, therefore, was considerably less than 0.000070°, and this includes, besides the errors of the electrical system, the effects of uncertainties in jacket temperature and in measuring it, of variations in stirring, and of the observer's possible failure always to estimate tenths correctly. This result was reached without using a thermostat, and in a room of very changeable temperature.

8. Experimental Details.

(a) *The Comparison, or "Cold" Calorimeter.*—Where a single jacket is used, the vacuum-jacketed comparison calorimeter can be immersed in it, just outside the chamber holding the working calorimeter, and can be covered with the same cover, as is partly shown in Fig. 3. In our own

[1] "Lag Effects and Other Errors in Calorimetry," Walter P. White, *Phys. Rev.*, **31**, 575 (1910).

work the comparison calorimeter was in a separate jacket. An attempt was made to secure complete uniformity of temperature around the calorimeter by means of a cover of very thick copper, but a more certain, more effective, and easier way of accomplishing this result afterward seemed to be by means of the double walled "water cap" shown in Fig. 1. This was made by a tinner for about $4.00, and was at once ready for use. Filled with water, and with one opening placed over the jacket stirrer, it provides abundant circulation above the calorimeter, and, touching the open water on all sides, it absolutely excludes air currents from the inclosed space. The thermoelement, as it runs to the calorimeter, dips down under this cover, and thus passes for some distance through the water. This arrangement can be made to prevent any influence of the room temperature upon the calorimeter. A reciprocating "bucket" stirrer is used (that is, a long

A.

B

Fig 1 —Copper "water cap," which helps secure a uniform temperature completely surrounding the cold calorimeter. A, Perspective; B, Sectional View, with a calorimeter, etc. An auxiliary thermoelement is omitted to simplify the drawing.

tube with a light hinged valve), which can be operated by rods passing up from below through the water, and therefore without complicating the cover.

Evaporation under the water cap can be prevented by pouring a layer

of heavy oil on the water in the calorimeter, and then keeping the calorimeter always a little warmer than the jacket. When evaporation was permitted, however, it only increased the cooling rate 20%, and it must become constant very quickly in the small inclosed body of saturated air, so it is allowed to occur unhindered.

Fig. 2.—"Submarine" arrangement of cold calorimeter, accomplishing the same object as the water cap.

Another arrangement of the comparison calorimeter was tried, and is shown, somewhat improved, in Fig. 2. The cover, a sort of diving bell, is borne by the thermoelement case. The insertion of the thermoelement carries down the air which fills this bell and surrounds the neck of the calorimeter.

Here the calorimeter temperature automatically becomes equal to that of the jacket whenever the thermoelement is removed.[1]

(b) An Inexpensive Complete Jacket.—The water cap just described serves, with a little modification, as the most characteristic part of a completely inclosing jacket for working calorimeters, and this deserves description here, since the value of the "Compensated Calorimeter Method" is somewhat dependent on the ease with which complete inclosure can be attained. An installation now in process of construction has the following essentials (Fig. 3): (1) For the outer vessel a commercial paper tub is used, which of course reduces expense. (2) Two metal bars crossing this tub at the top serve to support the inclosure of the calorimeter chamber. (3) This inclosure consists of two parts. The lower part is a nearly plain pot of suitable shape, which ordinarily remains fixed in position, though it can be changed, if desired, when a change is made in the working calorimeter. (4) The upper part, or jacket cover, is a parallelipipedal box,

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[1] This of course supposes that the stirrer is operated when the calorimeter has become colder than the jacket. In this case it may be desirable or necessary to insert a wide, short tube temporarily in the mouth of the bottle, to assist the stirrer in bringing the colder water well out of the bottle.

closed except for two large pipes, projecting downward like the horns in the water cap of Fig. 1, and of similar function. This cover can be slid about at will upon the cross bars, and will ordinarily serve for all the different calorimeters used.[1] (5) The power for the stirring may be brought into the chamber in various ways, according to circumstances. In our case the cover is in two parts, one of which is clamped fast during
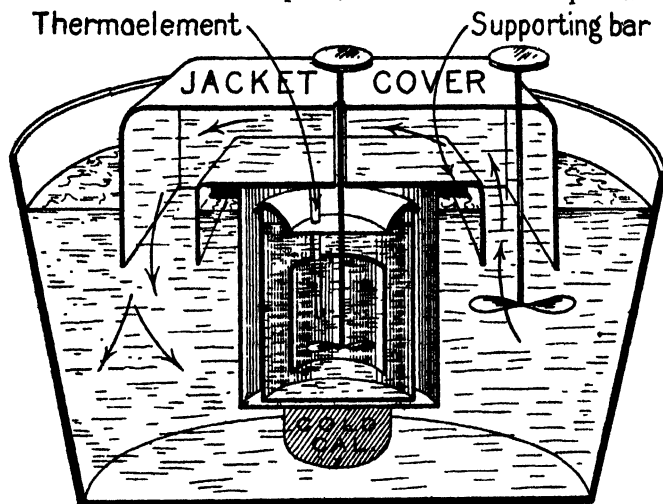
Fig. 3 —Complete inclosure of uniform temperature surrounding an ordinary calorimeter. Here the cold calorimeter, situated beyond the calorimeter-chamber shown, is covered by the same cover

a determination, and carries the stirrer pulley and connection, while the other part is at all times freely movable.[2] (6) For a thoroughly complete inclosure the jacket water temperature must prevail up to the very

[1] With a tub as small as that shown in Fig. 3 there would not be room to move the covers back far enough to expose the calorimeter. In general, a larger tub can be used, with advantages in several directions. In adiabatic work a small tub will usually be much more desirable. With it the covers are emptied and lifted off, and then refilled when replaced. The filling and emptying are done by sucking or blowing air through an inverted siphon; the procedure is thus not at all troublesome. If the resulting rise in the water level in the tub is objectionable, it can be avoided by removing water before the emptying of the cover, returning the same after filling. The level thus remains the same except during the filling or emptying, when it is low. A convenient way of removing the water is to transfer it into an inverted vessel (not here shown) somewhere inside the tub, making the transfer, again, by means of an inverted air siphon. The siphon tubes should be about a centimeter in diameter; the transfers are then almost instantaneous.

[2] An arrangement of this sort, applied to a more elaborate, but no more effective, jacket installation, has already been described, in "Some Calorimetric Apparatus," Walter P. White, *Phys. Rev.*, 31, 673 (1910).

top of the side wall of the calorimeter chamber. This has generally been secured by bringing the water up to the top of the side wall, which is a little troublesome, but is a slight price to pay for absence of all uncertainty as to the jacket wall temperature. Fortunately, however, a suffi-

cient and very certain uniformity of temperature in the jacket wall can be attained as follows: (Fig. 4): The upper 4 cm. or more of the wall is of (or is reinforced with) copper, about 1.5 mm. thick, and does not project more than 3 cm. above the water surface; outside of this and 4 or 5 mm. from it is a shielding rim whose lower edges turn outward 2 cm. or so in the water, so as to touch the water abundantly without keeping it from the true rim. This shielding rim, coming nearly to the temperature of the water, prevents the true rim from being sensibly affected by the room temperature, whose changes will cause not over 0.0005 as much change in the true rim. The lag of the very top of the rim will not be over 4 seconds, which is negligible even in the

Fig. 4.—Arrangement of shielding rim preventing the influence of the room temperature upon the upper part of the wall of the calorimeter chamber.

most accurate work, since it affects only a small part of the whole calorimeter chamber wall. The shielding rim does not appear in Fig. 3 because it is not needed under the ends of the jacket cover.

If a cold calorimeter is used in the same jacket, the copper rim may surround it also.

If the thermoelement then passes directly from one chamber to the other, evaporation into the working calorimeter chamber can be prevented by packing the orifice through which the thermoelement passes with plasticine or other soft wax, or else by pouring heavy oil on the water surfaces inside and outside the cold calorimeter.

Prevention of evaporation is recognized as important in thermostats of precision, and it is of course desirable or necessary for the jacket water with the type of installation just described. A quick and easy way to secure it is by casting paraffin on the surface of the water. The paraffin will not continuously support much weight, and hence must be supported, either by the water or otherwise. It is a good plan to use fixed paraffin to fill in around corners and irregularities, leaving the large, clear spaces protected by bodies of simple outline, either floating or otherwise supported.

It is an advantage to paint the jacket vessel white inside, which makes objects in it far more easily visible. The paint may be protected by a thin layer of paraffin.

(c) *Lever Adjusters.*—Some adjustment of the amount of water in the

calorimeters is desirable or necessary in nearly all calorimetric work. With the compensated calorimeters the quick method of Dickinson and George[1] gives more than sufficient precision and will often save a tedious adjustment of the weight on a balance. This method consists in sucking out excess water down to a desired level. The level reached is more constant, however, if the tube used is of different shape from that of Dickinson and George. Fig. 5 shows the adjuster used with our working calorimeter. It is made of a large cork, three nails and a little glassware. The nails, serving as a gage, rest on the calorimeter rim when the adjuster is in use.
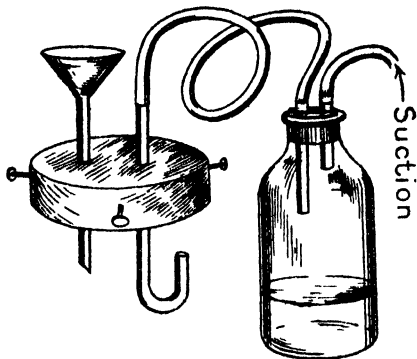
Fig 5.—Apparatus for quickly adjusting the water level in calorimeter.

(d) *Temperature Adjustment.*—The required adjustment of the temperature of the cold calorimeter to approximate equality with that of the jacket is practically the only special manipulation called for by the compensated calorimeter system, once the installation is completed. With the submerged cold calorimeter, this adjustment, as already pointed out, is nearly automatic. With a cold calorimeter not submerged, the adjustment is readily made on a similar principle, by sucking out the water into a large bottle, and then refilling from the jacket. If the jacket is made into a thermostat, these manipulations become unnecessary.[2]

9. Essentials of a Differential Calorimeter Installation.

The essential apparatus of the calorimetric system described in the present series of papers are here listed together.

A. *Calorimetric Arrangements.*

I. The *calorimeter* proper, or "working calorimeter," has no restrictions placed upon it by the differential methods here presented.

II. The *cold*, or *comparison calorimeter*, which is merely a vacuum jacketed bottle, and

[1] H. C. Dickinson, E. F. Mueller and E. B. George, "Specific Heats of Some Calcium Chloride Solutions between —35° C. and +20° C.," *Bull. Bur. Standards,* **6,** 388 (1910).

[2] As to the complication involved in this procedure it may be said that even in the most unfavorable case, where the cold calorimeter has a separate thermostat all to itself, the installation of the thermostat is simpler, and its maintenance less objectionable, than of the oil-filled thermostat around the Wheatstone bridge, which is generally considered the most desirable means of insuring high precision with the resistance thermometer.

11. Precautions and Safeguards.

This section gives, with an attempt at completeness, a list of features which must be provided in the apparatus, and of precautions which must not be forgotten in daily work, for observations of precision.

I. Features Required in the Apparatus.

(*1*) *Generally necessary—that is, not peculiar to the differential thermoelectric, compensated calorimeter method.*

A. Pertaining to the Calorimeter.

(*a*) Control of, or preferably prevention of, evaporation from the calorimeter.

(*b*) Sufficiently vigorous stirring in the calorimeter and especially in the jacket.

(*c*) Sufficiently constant speed of stirring in the calorimeter.

(*d*) Reduction of certain lag errors, which are usually negligible, but should not be assumed to be so.[1]

(*e*) (Occasionally) provision against excessive evaporation or other detriment to uniformity in jacket temperature.

B. Thermometric.

(*f*) To have sufficient depth of immersion of the thermometer.

C. Electric.

(*g*) To provide adequate insulation at all points.

(*h*) To provide equipotential leakage shields if necessary.

(*i*) To have it definitely known how much attention is needed by dial and other contacts.

(*k*) To have the coil corrections, if any, properly determined (usually there will be none).

I (2) Features Required in the Apparatus, Peculiar to the Compensated Calorimeter Method.

A. Pertaining to the Calorimeter.

I. Provision against friction of the cold calorimeter stirrer against the thermoelement.

II. Provision against appreciable heat of stirring in the cold calorimeter (or else against an appreciable difference between the two calorimeters).

B. Thermometric.

III. (In divided installations only) to have a copper temperature shield over the horizontal part of the thermoelement, to protect thermoelement and calorimeter from the effect of room temperature.[2]

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[1] *a* to *d* are discussed in: "Lag Effects and Other Errors in Calorimetry," *Loc. cit.* Irregular heat conduction to the calorimeter along the thermometer, which is troublesome with some electric thermometers, is, of course, impossible in the differential thermoelectric method with a single jacket, since the thermoelement is then completely included; and is prevented in divided installations by the sheet copper shield over the exposed portion of the thermoelement. A good thermal contact with the jacket where the thermoelement passes through may give additional security; it has proved sufficient by itself under severe tests.

[2] The observer should, of course, by all means, see to it that his thermoelement is sufficiently homogeneous at the place where the temperature gradient comes, but this amounts merely to saying that he must have a satisfactory thermometer, so I have not classed it as a precaution.

C Electric

IV. To have neutral (i e, practically, copper) wires and contacts outside of the eliminating switch

V. To have an eliminating switch which has been thoroughly tested for neutrality

VI To have some provision against the effect of direct sunlight, or heat from lamps, upon neutral switches or contacts

II Precautions Needed in Operation

(1) Not Peculiar to the Thermoelectric Methods

A Pertaining to the Calorimeter

(l) To avoid moisture on the working calorimeter

(m) To have the right amount of water in the same

(n) To see that the jacket stirring does not accidentally become too slow, from slipping of the belt for instance

(o) To see that the proper speed of calorimeter stirring is maintained [1]

(p) Not to overlook any change which may be produced in the heat equivalent of the calorimeter

B Thermometric

There are no general thermometric precautions which remain necessary when the compensated calorimeter method is used

C Electric

(q) and (r) To test insulation and shield whenever trying weather or other cause suggest the necessity [2]

(s) To Give the Contacts Needed Attention —(With the combination potentiometer this is almost nil if corrosive gases are absent   An overhauling twice a year will then prove more than sufficient)

(t) To avoid laying wires clothing, or other objects down so as to make a leakage path by the equipotential shield and to avoid letting live wires even if insulated, touch anything inside the shield in damp weather

II (2) Precautions Needed in Operation, Peculiar to the Compensated Calorimeter Method

A Calorimetric

VII. To let 10 minutes or so intervene between any considerable change in the cold calorimeter temperature (in adjusting it) and the beginning of observations

B Thermometric, nothing

C Electrical, nothing

Of these precautions n, o, q, r are the most troublesome, and their inconveniences are trifling   They are necessary for high precision by almost any method   The compensated calorimeter method itself evidently calls for practically no precautions

12. Availability of the Differential Thermoelectric Methods.

The intrinsic advantages of the differential thermoelectric system in calorimetry have been stated at the close of a previous paper [3]   They give rise to methods superior in absolute precision, certainty, and freedom from precautions, in quickness, and in the power of combining numer-

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[1] Our speed is governed and the governor operates by means of incandescent lights, whose winking shows when the governor is working properly

[2] The tests given in "Leakage Protection by Shielding, Especially in Potentiometer Systems" (Loc cit), will usually be sufficient in potentiometer systems

[3] "Potentiometers for Thermoelectric Work, Especially in Calorimetry," Loc cit

ous and varied observations. It will probably be clear from the present paper that the calorimetric arrangements necessary to secure these differential methods entail disadvantages which are slight, and are practically done with, once the original installation is accomplished. The same may be said of the electrical arrangements. The methods will therefore nearly always be satisfactory, even where they are not noticeably preferable. Wherever a variety of work is to be done the thermoelectric apparatus is likely to prove decidedly superior for some of it.

If apparatus is desired which can be made useful in work not calorimetric, the thermoelement installation will be useful not only for all thermoelectric work, including high temperature measurement, study of heat conduction, etc., but also for much potentiometer work where no temperature measurement is involved. For measurements which are naturally or necessarily differential (such as freezing point depressions, for instance) the thermoelement is especially advantageous. If, however, the electrical apparatus is likely to be needed for very accurate measurement of single temperatures (*i. e.*, not temperature intervals) as in determining fixed points with the highest precision, the resistance thermometer, which is more convenient for such measurements, is more likely to be preferable.

Summary.

In the calorimetric "Method of Mixtures," a precision approaching or reaching 0 1 per mille, though somewhat unusual, is often desirable, and is ordinarily not difficult to attain with appropriate apparatus Its attainment is especially easy with a two-calorimeter installation, which secures the convenience and high precision of differential thermoelectric temperature measurement. This is the only advantage of the two-calorimeter arrangement; the diminution of heat-loss error, often counted an advantage, turns out upon examination to be largely illusory. By abandoning the twin calorimeters previously used to get this supposed advantage, and using for the comparison calorimeter a vacuum jacketed flask, there is a gain in convenience and precision. A special thermoelement combination renders the necessary temperature observations as simple as with the twin arrangement. A completely inclosing jacket of uniform temperature is necessary for this method, but this is no loss, for such a jacket proves to be necessary for highest precision with any other method. This method is quite as effective with two jackets, one around each calorimeter, and therefore with adiabatic methods.

Efficient complete jackets can be very easily realized according to several methods, which are described.

As compared with others, the present method is especially advantageous for observations of great absolute precision, and wherever it is desirable to secure the advantages which the thermoelectric system possesses in the way of rapidity and of facility in making varied observations.

Apparatus especially valuable for this method is described in a series of papers, of which this paper is the last.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

ALTERNATING CURRENT ELECTROLYSIS.

BY JNANENDRA CHANDRA GHOSH.

PART I.

Manuevrier and Chappius[1] found that, when an alternating current is passed through electrodes of very fine platinum wires dipped into a sulfuric acid solution, there is an immediate and abundant evolution of gas. They also found that the higher the frequency the less the amount of decomposition.

Ayrton and Perry[2] used alternating currents having a frequency of 10,000 per minute, and made the interesting observation that a deposition of hydrogen gas on a platinum electrode hinders visible decomposition by alternating currents, while deposition of oxygen favors such decomposition. Hopkinson, Wilson and Lyddal[3] also investigated the nature of electrolysis by alternating currents, but they laid more stress on the physical side of the question. M. LeBlanc[4] passed an alternating current between copper electrodes in a cyanide solution and found that, with the rate of reversal of 1000 per minute, copper passed quantitatively into solution; while, with the rate of 38,000 reversals per minute, only 33% of the theoretical quantity dissolved. LeBlanc holds that the copper passes into solution if the copper dissolved at the anode has time to be converted into the complex cuprocyanide ion before the reversal of the current.

Brochet and Petit[5] do not share the view that the possibility of alternate current electrolysis depends on the formation of a complex ion. They conceive the general condition for the formation of a new compound to be, that the ion, on reaching the electrode, has had time to part with its charge before reversal produces the ion of the opposite charge. at the same electrode. Ostwald also holds the above view. It frequently happens that the immediate product of the chemical processes at the electrodes undergoes further changes which are difficult to reverse. He considers that reversibility is often merely a question of time and the short intervals of time is always present. This is shown by the fact that

[1] *Compt. rend.*, 106, 1719–22; 107, 37–40.

[2] *Electrician*, 21, 299–300.

[3] *Proc. Roy. Soc.*, 54, 407–417.

[4] *Z. Elektrochem.*, 11, 705 (1905).

[5] *Ibid.*, 10, 909 (1904); 11, 441 (1905).

in using alternating currents to measure electric conductivity no deviation from Ohm's law has been observed. This proves that the energy of one current which has disappeared in polarizing the electrodes reappears in the next current of opposite direction, i. e., the chemical decomposition effected by the passage of the alternating current in one direction is completely reversed by the succeeding identical current in the opposite direction, and the resultant chemical action thus becomes nil. The direct experimental verification of this view is, however, a very difficult one, since, even if any chemical action takes place on the passage of a high frequency alternating current through an electrolyte, it will be so minute that our ordinary methods of chemical analysis would fail in detecting it. It occurred to the author that by measuring the potential differences between an electrode and an electrolyte, before the passage of an alternating current, and then during or just after the passage of the same, a clue might be obtained as to whether any chemical action has taken place on the electrode surface. It was also thought possible that, since the electrode potential is due to the electrical double layer at the surface of separation between the electrode and the electrolyte, the amount and direction of variation of electrode potential may throw light on the nature of the chemical changes at the electrode surface.

The following method of experimental procedure was adopted: A B is a potentiometer wire (see Fig. I) through which a constant current from
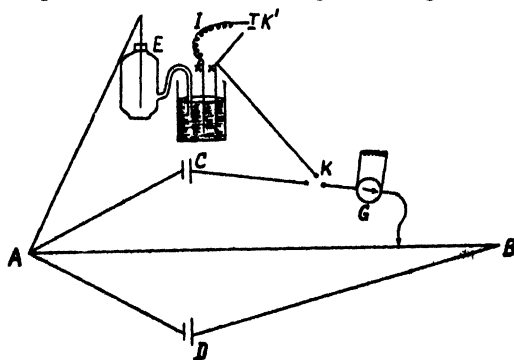
Fig I.

a four-volt battery D is passing C is a Weston cadmium element and E is a decinormal calomel electrode of comparatively high resistance. X and X′ are the electrodes dipped into the electrolyte whose electrolysis on the passage of an alternating current is to be studied. They are joined through a key, K′, to the two terminals of the secondary I of an induction coil. The key K′ consists of a mercury cup in which the two connecting wires are dipped, and should be placed nearby on the potentiometer table. Since it is necessary to measure the electrode potential of either X or X′ just after the passage of an alternating current, the time between breaking contact at K′ and making the galvanometer contact with the potentiometer wire should not be at all appreciable. The induction coil

used is a very small one, such as is generally used in the conductivity measurements according to the method of Kohlrausch. The frequency of alternation was 30,000 per min. approximately. The current passing through the primary was measured by an ammeter placed in the circuit. K is a three-way key and G a galvanometer. The galvanometer was shunted off by means of a sliding resistance (which should be near at hand). The E. M. F. of the combination E and X is measured by comparison against C.

The first experiments were carried out to determine whether there is any variation in the electrode potential on the passage of an alternating current through two pieces of the same metal dipped in its own salt solution. Two clean zinc rods were taken and immersed in a normal solution of zinc sulfate. The internal resistance of the cell thus obtained was about one ohm. The current strength through the primary of the induction coil was $^3/_{15}$th of an ampere.

E. M. F. of the combination of E and X before the passage of the alt. current = 1.105 volt.

E. M. F. of the combination of E and X during to passage of the alt. current = 1.105 volt.

E. M. F. of the combination of E and X just after the passage = 1.105 volt.

The same constancy of behavior was obtained in the case of cadmium in cadmium sulfate solution and copper in copper sulfate solution. In the case of metals dipped in their own salt solutions such constancy of behavior is to be expected, for here the question of an irreversible change being conducted reversibly does not come in. These results also justify the assumption that only when there is some such change as would alter definitely the chemical nature of the electrical double layer, is its effect noticeable by the measurements of the electrode potentials.

The next investigation carried out consisted in determining the changes in the electrode potentials in cells consisting of two platinum electrodes dipped in any electrolyte. The great disadvantage of these determinations lies in the fact that we seldom get a constant value of the electrode potentials in these cases, and therefore these measurements cannot be exactly repeated. But, since the variation of electrode potential is the only point of importance, the uncertainty in the absolute values of these potentials does not affect the worth of these measurements. Two pieces of polished platinum of equal area—3.5 cm. in length and 1 cm. in breadth, were cut out from the same foil, cleaned, ignited red hot and then kept dipped in the given electrolyte for about 24 hours. It was found, in accordance with the observation of Smale[1] and others, that, in order to obtain a maximum constant potential difference between the electrodes and the electrolyte, it is necessary to keep the electrodes immersed in the

[1] Z. phys. Chem., 14, 577 (1894).

given solution for quite a long time. The electrodes were washed and ignited red hot each time they were used for potential measurements

TABLE I

Acid	Concentration	E M F before passage	E M F during passage	E M F after passage
HCl	1 0 N	+0 52	+0 31	+0 35
HNO₃	1 0 N	+0 68	+0 48	+0 52
CH₃COOH	0 2 N	+0 25	—0 02	—0 01
HCOOH	0 2 N	+0 07	—0 37	—0 30
COOH | | COOH	0 2 N	+0 31	—0 02	+0 01
H₂SO₄	0 2 N	+0 51	+0 61	+0 60
H₂CrO₄	1 0 N	+0 80	+0 96	+0 92
Monochloroacetic	0 2 N	+0 31	+0 60	+0 57
Trichloroacetic	0 2 N	+0 35	+0 52	+0 49
Lactic acid	0 2 N	+0 34	+0 51	+0 50
Tartaric acid	0 2 N	+0 34	+0 54	+0 52
Malonic acid	0 2 N	+0 35	+0 61	+0 60
Malic acid	0 2 N	+0 31	+0 42	+0 39
Citric acid	0 2 N	+0 36	+0 58	+0 54
Benzene sulfonic acid	0 2 N	+0 34	+0 54	+0 51

TABLE II

Potassium hydroxide	1 0 N	+0 05	—0 02	+0 01
Sodium hydroxide	1 0 N	+0 06	—0 02	+0 01
Sodium carbonate	0 1 N	+0 09	+0 02	+0 03

TABLE III

Potassium permanganate	0 1 N	+0 45	+0 54	+0 49
Potassium dichromate	0 1 N	+0 35	+0 45	+0 41
Potassium nitrate	1 0 N	+0 2	+0 30	
Potassium chlorate	1 0 N	+0 22	+0 31	
Potassium bromate	1 0 N	+0 35	+0 43	

TABLE IV

Hydroxylamine hydrochloride	1 0 N	+0 02	—0 05	—0 01
Hydrazine sulfate	1 0 N	—0 13	—0 18	—0 16
Sodium sulfite	1 0 N	—0 16	—0 21	—0 17
Potassium iodide	1 0 N	+0 10	—0 08	+0 05

TABLE V

Salt	Concentration	E M F before passage	E M F during passage	E M F after passage
Potassium chloride	0 N	+0 15	+0 30	+0 25
n bromide	0 N	+0 12	+0 26	+0 27
sium sulfate	0 N	+0 15	+0 21	+0 20
sulfate	0 N	+0 14	+0 28	+0 21
Copper sulfate	0 N	+0 30	+0 38	+0 36
Zinc chloride	0 N	+0 21	+0 40	+0 38
Sodium tartrate	0 N	+0 05	+0 024	+0 03
Sodium citrate	0 N	+0 11	+0 21	+0 20
Chromium sulfate	0 N	+0 41	+0 50	+0 48

against a fresh solution. The electrodes were kept 1 cm. apart, and an alternating current passed for 15 min. The current strength through the primary was $^2/_{15}$th of an ampere. The E. M. F. was measured just before the passage of the alternating currents during the passage, and then just after the stoppage of the alternating current. The secondary circuit was always kept closed.

It was found that, although the absolute values of the E. M. F. depend much on the concentration of the electrolyte, the amount of variation of E. M. F. is much the same for all concentrations between 1.0 N and 0.1 N. The variation depends much on the time of the passage of the current, rising to a maximum after a definite interval which did not exceed 15 minutes in any of the cases studied. In the tables, therefore, the maximum variation has been noted down. The negative values of E. M. F. in the tables mean that in these cases the calomel electrode is positive. It will be noticed that, in all the cases recorded above, the

E. M. F. just on stopping is nearer the initial E. M. F. than the E. M. F. during the passage of the alternating current. Indeed, in all the cases investigated, a complete recovery curve was obtained. They are all similar in nature and only some of the typical ones are given in Figs. II, III and IV. It will be noticed that, in the beginning, the recovery is quite rapid but afterwards it becomes quite slow. The fact that in each case the E. M. F. gets back to the original value goes to show that they are tending towards stable conditions. The new chemical substances produced by the action

Time in minutes
Fig. II.

of the alternating current alters the nature of the electrical double layer, but they soon disappear by diffusion and we get the old values of the E. M. F. again.
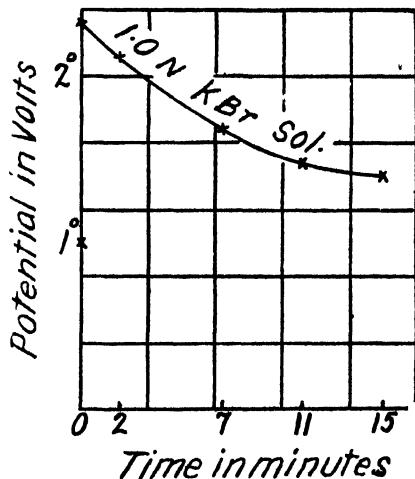
On examination of Table I, it will be noticed that the acids may be divided into two groups. For the acids 1–5 the E. M. F. diminishes on the passage of the alternating current, while for the rest the opposite is the case. The latter class of acids are all characterized by either containing Cl or (OH) groups. Thus the behavior of lactic, tartaric, or monochloroacetic acids is quite different from that of formic, acetic or oxalic

acids. It will also be observed that the E. M. F. of acids undergoes greater variation that the E. M. F. of other electrolytes—the amount of variation being from 0.2 to 0.4.

In Table II it will be observed that the variations are in the same direction—the E. M. F. diminishing during the passage of the alternating current. The variations here are also relatively small.

In Table III all the substances are oxidizing agents and we find that the E. M. F. increases during the passage of the alternating current. With the reducing agents the contrary is the case—the E. M. F. diminishing during the passage of the current.

In the case of the salts e. g., potassium chloride, sodium chloride, the E. M. F. generally increases with the passage of the alternating cur-
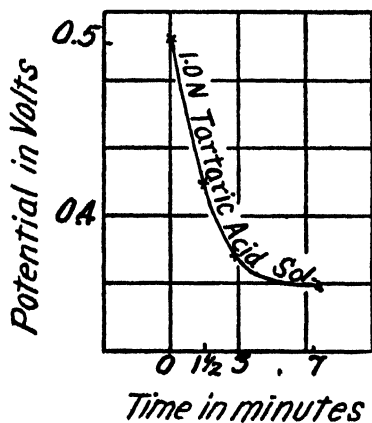
Fig. III.
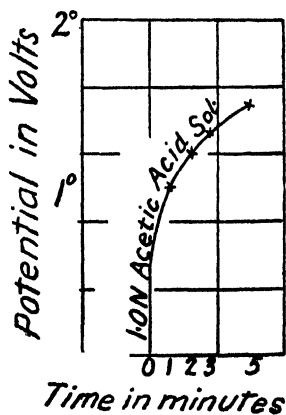
Fig. IV.

rent. Now the electrode potential observed on the platinum surface is always referred to as being the potential difference between the air and the solution, or more particularly between the oxygen gas of the atmosphere and the O″ or OH″ ions of the solution. A diminution in the value of the electrode potential must therefore be attributed to a diminution in the concentration of the oxygen gas. We may expect a diminution of the value of the electrode potential on the passage of an alternating current in the case of platinum foils dipped in solutions of reducing agents, if we believe that the anion of the electrolyte breaks up at the electrode surface and combines with the oxygen there to form more stable bodies. The diminution of electrode potential in the case of certain acids is also intelligible on the assumption that the discharged hydrion goes to combine with the oxygen of the double layer. . Similarly, by assuming the decomposition of the anion of an oxidizing electrolyte and the consequent setting

free of oxygen gas, we may explain the increase in the electrode potential observed in those electrolytes. The above variations in electrode potential therefore give us a direct experimental evidence of the fact that on a polished platinum surface, even for such short intervals of time as $1/2 \times 30000$ minute, the chemical process at the electrode is not a reversible one, i. e., the ion has had time to part with its charge and form other more stable bodies

When the platinum electrodes in the previous cases were substituted by mercury electrodes, a good deal of the variation in the electrode potential on the passage of the alternating current was also noticed Here, however, it is very difficult to obtain fairly concordant results, even after taking all the precautions used in the case of platinum electrodes Here the electrolytic cell of the previous cases was replaced by a H shaped cell, at the bottom of the two limbs of which there is a sufficient quantity of pure mercury to act as electrode The cross-section of the surface of mercury was 0 75 cm sq and the distance between the surfaces of the electrodes 1 2 cm.

TABLE VI

Electrolyte	Concen tration	E M F before passage	E M F during passage	E M F after passage
H_2SO_4	1 0 N	+0 20	+0 23	+0 22
HCl	1 0 N	+0 11	+0 15	+0 12
$K_2Cr_2O_7$	0 1 N	+0 272	+0 32	+0 31
$Na_2S_2O_3$	0 1 N	—0 40	—0 51	—0 42
KI	0 1 N	—0 46	—0 49	—0 48
Na_2SO_3	1 0 N	—0 05	—0 06	—0 05

The amount of variation to be observed in these cases is not so great as in that of platinum. The nature of variation is also, in many cases, quite unlike that of platinum. The peculiarity was observed that after the passage of the alternating current the mercury surface in most cases lost its brilliancy, and it was therefore suspected that some chemical compounds might have been formed Indeed Manuevrier and Chappius[1] noticed that when an alternating current was passed through mercury electrodes in sulfuric acid solution there was formation of mercurous sulfate on the electrode surface.

When, however, electrodes of platinum black are used the above variation in electrode potection on the passage of alternating currents almost disappears. In no case were the fluctuations more than 0 015 volt. This proves that there is no appreciable consumption of energy at the electrode surface and the condition which Ostwald lays down for the trustworthiness of conductivity measurements by means of alternating current is almost fulfilled.

[1] *Loc. cit.*

The variations, under the influence of alternating currents, of the single electrode potentials of combinations which have an E. M. F. of their own was next studied. Here it is impossible to observe the fluctuations in electrode potentials during the passage of the alternating current, for there the two dissimilar electrodes are in metallic contact through the secondary of the induction coil. The readings are therefore taken for each electrode, before and just after the passage of the alternating current—the arrangements, as has been previously mentioned, being such that no appreciable time passes between the breaking of the secondary circuit and the determination of the null point. A completely reversible element shows no peculiarity, inasmuch as the electrode potential remains absolutely the same before and after the passage of the alternating current.

The study of cells containing an electrode consisting of a metal surrounded by its insoluble salts gave quite interesting results. In this type of cells, which have an E. M. F. of their own, the electrode gets polarized when the cell is allowed to work for itself. Here, in order to determine the effect of the alternating current, it is necessary to study first the behavior of the cell as regards its E. M. F. after it has been allowed to work for itself for a certain amount of time; the cell is then left to itself to recover its normal condition, and when the recovery is complete it is again allowed to work for the same interval of time under the influence of an alternating current, and its behavior as regards E. M. F. again studied. The Helmholtz calomel element, zinc-zinc chloride-mercurous chloride-mercury, was taken up for study. The cell, after preparation, should be left to itself for a few days, so that mercurous chloride may settle completely and in a compact condition on the surface of mercury. This is necessary in order to secure standard conditions as regards the depolarizing capacity of the cell. The electrodes of the cell were corrected through a resistance box and the mercury cup K' to the two terminals of the secondary coil. Here there is no necessity of the calomel electrode, A and B being directly connected to the electrodes of the calomel element.

Initial E. M. F. of the cell = 1.02 volt. The circuit is closed through a resistance of 460 ohms. E. M. F. of the cell just on breaking circuit after 10 min. 0.61 volt. The cell is allowed to recover, and then after 2 hours, external circuit is closed with an alternating current passing through the secondary coil—the current strength through the primary being $^1/_{11}$th of an ampere. E. M. F. of the cell just on breaking circuit after 10 min. = 0.15 volt. By varying the external resistance, different reading for the two sets of values of E. M. F. could be obtained. The circuit is kept closed in each case for 5 minutes.

TABLE VII.

Resistance. Ohms.	Initial E. M F Volt	E M. F. after closing circuit simply	E M F. after closing circuit with an alt. current
400	1.02	0 51	0 12
700	1 02	0 76	0 16
900	1 02	0 84	0 20
500	1 07	0 45	0 11
700	1 07	0 64	0 16
900	1 07	0 81	0 20

TABLE VIII.

Resistance Ohms	Initial E M F Volt	E M F after closing circuit simply	E M. F. after closing circuit with an alt current
200	0 8	0 49	0 26
300	0 8	0 18	0 16
500	0 8	0 19	0 16

In the cell whose E. M. F. was 1 07 volt the zinc chloride solution was more dilute. The recovery curve could also be easily traced in the case where the external circuit was kept closed through a small resistance for about 15 minutes. Fig V shows a typical one The rate of recovery

Fig V
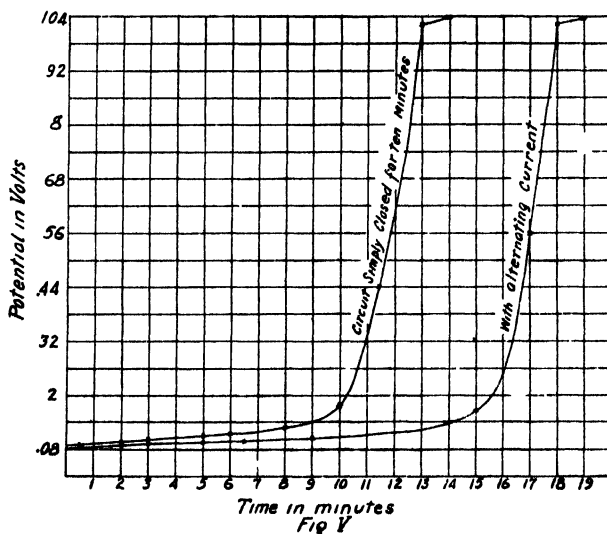
is slow at the beginning, very rapid after some time, and then again slows down as the normal E. M. F. is approached. The curve in the case where no alternating current passed is always above the curve of the case where the alternating current did pass.

The cell Cd–CdCl$_2$–Hg$_2$Cl$_2$–Hg also lends itself to study in the same manner.

The recovery curve is given in Fig. VI. It will be noticed that in the case of these cells, even when there is sufficient resistance in the external circuit, the rate of recovery is slow enough to be accurately traced.

The cell zinc-zinc sulfate-mercurous sulfate-mercury was also studied.

The external resistance in the circuit should be as small as possible, mercurous sulfate being soluble enough to give unpolarizable electrodes for small current densities. In this case, the recovery curves are similar to those of the calomel cell. Now, since in all the cells studied, there remained always a sufficient amount of mercury salt on the surface of the

Fig VI
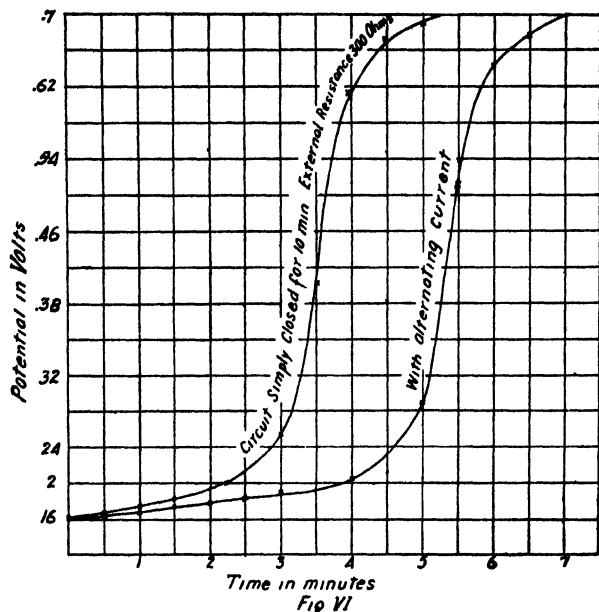
mercury electrode, we may reasonably hold that the depolarizing capacity of each cell retained a constant value. Now the curves of recovery to the normal E. M. F. with time, as also the values of E. M. F. just on the breaking of circuit, show unmistakably that the cell retains its polarization longer in the case when an alternating current plays in the external circuit than in that in which the external circuit is simply kept closed. If therefore we attribute a constant value to the depolarizing capacity of each cell we may conclude that a greater amount of polarization takes place in the former case than in the latter.

The effect of impressing an alternating current to the above type of cells is therefore to increase the amount of polarization at the mercury electrode, and necessarily to increase the amount of the polarizing current which the cell furnishes of itself.

The behavior of cells containing an electrode which is very easily polarizable was next studied. The internal resistance of the cell was always very small—never greater than one ohm.

TABLE IX.

Cell	E M F before passage	E M F after simply closing circuit	E M F after closing circuit with alt current
Zn ZnSO₄ Pt	1 41	0 05	0 05
Cu-CuSO₄ Pt	0 31	0 04	0 04
Cd CdSO₄ Pt	1 20	0 05	0 05

TABLE X.

Cell	E M F of the mercury electrode	
	Before passage	After passage of alt. current
Cd-ZnSO₄ Hg	—0 05	+0 98
Al-ZnSO₄ Hg	—0 07	+1 01
Fe ZnSO₄-Hg	—0 06	+1 02
Ni ZnSO₄ Hg	—0 1	+1 00
Ca ZnSO₄ Hg	—0 08	+0 10

Quite a number of such cells were studied, but in no case was a great difference found between the values in the 3rd and the 4th column   The rate of disappearance of polarization with time did not yield reliable results   However, in the case of those cells where mercury is the polarizable electrode, e g , zinc zinc sulfate mercury, magnesium magnesium sulfate mercury, it is observed that ripples begin to play more violently on the mercury surface when an alternating current plays in the external circuit

The next type of cells consisted of electrodes both of which were easily polarizable   The electrode potential of each electrode of the cell was measured against a decinormal calomel electrode, before and then just after the passage of the alternating current   The salt solutions used were quite concentrated and the internal resistance of the cell was, as in the previous ones, very small   The alternating current was allowed to pass for 15 minutes

Except in the case of nickel, the electrode potential of the more electro positive metals of the above cells did not change appreciably   In the case of the cell Ni-ZnSO₄ Hg the electrode potential of nickel rises from +0 24 to +0 42, but this high value is not retained long enough   In all the above cells, except in the case of the cell Cu ZnSO₄ Hg, it will be observed that the mercury electrode assumes a potential value which is almost equal to that of metallic zinc against a zinc sulfate solution   Evidently zinc has formed an amalgam with mercury   The mercury electrode loses its high E M F only very slowly

TABLE XI.

Cell	E M F of the platinum electrode	
	Before passage	After passage of the alt current
Cd-ZnSO₄-Pt	—0 25	+0 95
Fe-ZnSO₄-Pt	—0 22	+0 56
Ni-ZnSO₄ Pt	—0 23	+0 62

TABLE XII.

Cell	E M F of mercury electrode	
	Before passage	After of alt current
Ni CdSO₄ Hg	—0 12	+0 62
Fe-CdSO₄ Hg	—0 15	+0 63
Ca-CdSO₄-Hg	—0 16	+0 60

It is to be noticed that the platinum electrode attains the E M. F. of zinc only in the case of the cell Cd-ZnSO₄-Pt   Unlike the behavior of the mercury electrodes, platinum does not retain this high potential for

a long time. Fig. VII is a typical recovery curve of the platinum electrode in the case of the cell Cd-ZnSO₄-Pt. The two breaks at 0.83–0.86 volt and again at 0 2–0.25 volt are very peculiar. The first break perhaps indicates the lower limit of existence of zinc and the other at 0.23, the
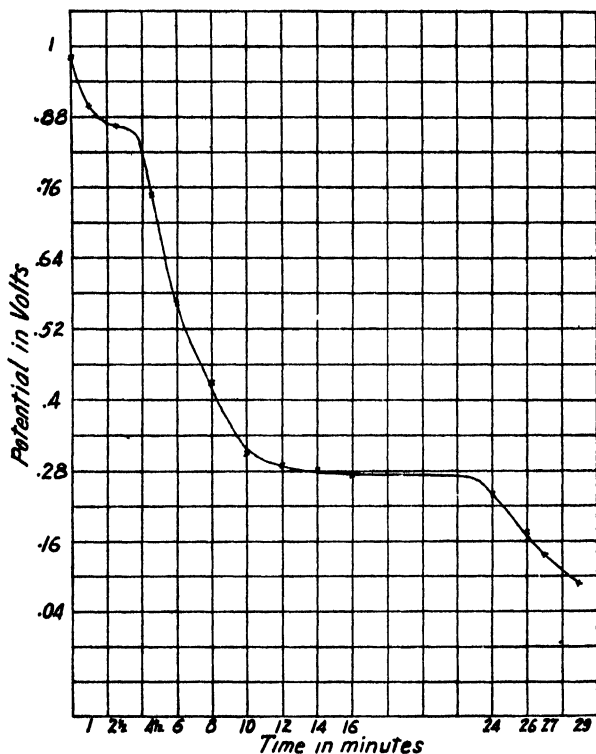
Fig. VII.

existence of hydrogen gas which is perhaps evolved by the solution in water of zinc deposited or the platinum surface. In this connection the work of Oberbeck[1] and Königsberger and Muller[2] on the concentration of the massive metal, may be referred to. Cells were then studied in which the electrolyte was a salt of cadmium.

In all the above cases the electrode potential of mercury, after the passage of the alternating current, approaches the potential value of cadmium against cadmium sulfate solution. Here also mercury loses its high E.M.F. only very slowly. In the cell Cu-CdCl₂-Hg, mercury did not

[1] Wied. Ann., 31, 336 (1887)

[2] Phys. Z., 6, 847, 849 (1905).

exhibit the E. M. F. of cadmium, and the contrast between the behavior of the two salts is quite marked.

TABLE XIII.

| | E. M. F. of the platinum electrode | |
Cell.	Before the passage.	After the passage of the alt. current.
Ni-CdSO$_4$-Pt........	—0.26	+0 61
Cu-CdSO$_4$-Pt........	—0 25	+0.02

Platinum in the case of the first cell approaches the potential value of cadmium, but not in the case of the second cell. However, the cell Ni-CdSO$_4$-Pt shows quite an anomalous behavior. The behavior of the platinum electrode of the cell depends essentially on the condition of the nickel electrode. If the alternating current be passed through the cell just after the nickel wire, thoroughly cleansed and polished with emery paper, is dipped into the electrolyte, platinum could be made to attain the potential value of cadmium. If, however, the alternating current is passed, several hours after the cell has been prepared, the E. M. F. of platinum rises from —0.27 to +0.01 volt. The behavior of nickel electrode itself also indicates this change in the condition of its surface on being kept dipped into the electrolyte. The E. M. F. of nickel against a decinormal calomel electrode just on dipping it into the solution was +0 2 volt, and after the passage of the alternating current for 10 minutes was 0.5 volt. However, if the electrode be kept immersed in the solution for several hours the initial value is only +0.08 volt, and that after the passage of the alternating current only +0 10 volt. No change in the surface of the nickel electrode could be observed with the eye

Some cells formed by the combination of two electrolytes were next studied. It has been stated before that when an alternating current passes through the cells Cd-ZnSO$_4$ sol.-Hg, Cd-ZnSO$_4$ sol.-Pt, the mercury or platinum exhibits the electromotive force of zinc. But the behavior of the cells Cd-CdSO$_4$-ZnSO$_4$-Hg, Cd-CdSO$_4$-ZnSO$_4$-Pt is quite otherwise. In no case could the value of the electrode potential of mercury or platinum be made to exceed the electrode potential of cadmium against cadmium sulfate solution. In cells of the type M-MX-M$_1$X-M$_1$, where M is the more electropositive metal, it was found that M$_1$, even under the influence of a fairly strong alternating current, could not be made to attain an electrode potential greater than that of M.

The cells Ni-ZnSO$_4$-CdSO$_4$-Hg, Ni-ZnSO$_4$-CdSO$_4$-Pt were next studied. It was observed that after the passage of the alternating current both mercury and platinum electrodes assumed the electrode potential of cadmium.

Further work on the nature of electrolysis under the simultaneous influence of a direct and an alternating current is in progress.

My thanks are due to Professors P. C. Ray and J. B. Bhaduri for their encouragement in carrying on the above investigation.

CHEMICAL LABORATORY, PRESIDENCY COLLEGE,
CALCUTTA.

EQUILIBRIUM IN THE SYSTEM: LEAD ACETATE, LEAD OXIDE, WATER, AT 25°.

BY RICHARD F. JACKSON.

The basic acetates of lead owe a considerable importance in applied chemistry to the fact that, for a large class of crude substances, they are the most effective and most convenient clarifying agents known. In the analysis of crude saccharine products the question of clarification is assuming an ever-increasing importance, as the sugar analysis approaches a continually higher precision. In order that further advances may rest upon a firm basis, it seems highly advisable that in place of acquiring more empirical data on the crude products themselves, we turn our attention to some of the more fundamental problems involved. The present work was undertaken in order to contribute to our very meager knowledge of the basic acetates themselves and their behavior in aqueous solution. Its application to the complicated problem of sugar clarification will form the subject of a special investigation.

A glance into the history of the study of this problem reveals the fact that while a number of compounds have been reported, no work has been done in the light of modern knowledge. Much of the work which has hitherto been accepted was done under assumptions which we now know to be radically erroneous. As an instance of this the work of Löwe[1] may be cited. This investigator boiled lead oxide and lead acetate for an arbitrary length of time and, upon obtaining a solution and a residue, he assumed that each represented a compound. In order to identify these compounds he used them to precipitate the insoluble basic nitrate of lead, which was then recrystallized before analysis. Its analysis was assumed to indicate the proportion of basic to neutral lead in the original compound. The conclusions based upon this procedure must be considered invalid.

In other instances investigators have attempted to isolate and purify the basic compounds and have reported the formulas on the basis of the direct analysis of these substances. In most cases the substance obtained must have been heterogeneous. Indeed, as will appear from the present work, it is almost, if not quite, impossible to isolate at least one of the basic compounds, while the danger of obtaining a mixture is so great that it makes this method of investigation unreliable.

[1] J. prakt. Chem., 98, 385 (1886).

The following compounds have been reported

$$Pb(C_2H_3O_2)_2 \, 5PbO^1$$
$$Pb(C_2H_3O_2)_2 \, 2PbO^2$$
$$Pb(C_2H_3O_2)_2 \, PbO^3$$
$$3Pb(C_2H_3O_2)_2 \, 2PbO^4$$
$$2Pb(C_2H_3O_2)_2 \, PbO \, H_2O^5$$
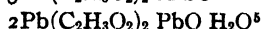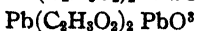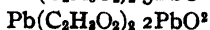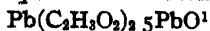
The U S Pharmacopoeia states that neutral lead acetate is soluble in two parts of water at 25° Other than this, no measurement of the solubility of neutral or basic lead acetate has been made

The present work has been intended to show what compounds exist and what are the limits of stability of each For this purpose the problem was attacked from the standpoint of the Phase Rule

Preparation of Reagents.

Lead Acetate —Lead acetate, C P , from Baker & Adamson, was recrystallized once from distilled water containing a slight excess of acetic acid Two samples were tested by separating the lead quantitatively as sulfate and sulfide, respectively The filtrate in each case yielded no significant residue

Lead Hydroxide —Recrystallized lead acetate was dissolved in water free from carbonic acid A small quantity of this solution was added to a caustic alkali solution and the mixture allowed to stand several days to permit lead carbonate to settle The solution was then filtered rapidly through asbestos and mixed with the remaining lead acetate solution The lead hydroxide precipitate was thrown on a filter and washed with water free from carbon dioxide until free from sodium salts The content of lead oxide was determined by ignition of a small sample This procedure could not have accomplished the complete elimination of carbonate, but a few experiments showed that the presence of even a considerable amount of carbonate was without influence on the equilibrium

Acetic Acid —The C P reagent of commerce was redistilled and the middle portion of the distillate reserved for use

Analytical Procedure.

The analytical processes were required to yield the percentages of neutral lead acetate and of basic lead present in the sample These data were obtained by measuring the quantity of standard acid neutralized by the basic lead and the quantity of reagent required for the complete precipitation of lead Two methods of estimation of total lead were utilized,

[1] Wittstein and Kuhn *Buchner s Rep* 84, 181

[2] Lowe *Loc cit* Pelouse *Ann* 42, 206 (1842)

[3] Lowe *Loc cit*

[4] Brown s Handbook of Sugar Analysis p 207

[5] Stolle Handbuch fur Zuckerfabriks Chemiker p 527, Wohler A 9, 63 (1839)

namely, precipitation by normal sulfuric acid[1] and precipitation by one-third normal sodium oxalate.[2]

To the weighed sample, in a 500 cc. volumetric flask, a slight excess of normal acetic acid was measured from a pipet. In the sulfate method the solution was diluted and sufficient normal sulfuric acid added for complete precipitation. The solution was made up to the calibration mark with water free from carbon dioxide, mixed and allowed to remain over night. Since the total precipitate of lead sulfate amounted to more than 15 grams, the quantity remaining in solution in the presence of the excess sulfuric acid was too small to be significant. Four 100 cc. aliquot portions of the clear supernatant liquid were drawn off in a pipet. Duplicate titrations were made with standard alkali to determine the excess of acid. The alkali was a solution of sodium hydroxide containing a little barium hydroxide. Phenolphthalein was used as an indicator. In the remaining two portions the excess of sulfuric acid was determined by precipitation with barium chloride. In this precipitation the precautions recommended by Allen and Johnson[3] were observed.

In the oxalate method the acetic acid was added in the same manner. An excess of third normal sodium oxalate was measured in and the solution made to volume, mixed, and allowed to settle. The aliquot portions of the supernatant liquid were titrated for free acetic acid with normal alkali and for excess of oxalate with potassium permanganate.[4] This method, on account of its greater convenience, was the main reliance. The two methods proved to be equally trustworthy. The lead oxalate is much less soluble than lead sulfate. The presence of the slight quantity of acetic acid did not appear to increase the solubility appreciably. The acetic acid was without influence upon the permanganate titration, provided it was purified by redistillation.

The volume of the precipitate was computed in every instance and deducted from the calibrated volume of the flask. For this purpose the data of Schroder[5] for the density of precipitated lead sulfate are available, but no data exist on that of lead oxalate. Consequently this was determined. The precipitated oxalate was washed by decantation and transferred to a calibrated pycnometer. The pycnometer was nearly filled with water, which was then brought to boiling in a vacuum to remove air. After adjustment and weighing, the contents of the pycnometer were transferred to a Gooch crucible and the weight of the dry precipitate

[1] Allen and Johnson, "Quantitative Chemical Analysis," Vol II, p 599 (1904).

[2] Classen, "Lehrbuch der Chemisch-Analytischen Titrirmethoden," 7th Aufl., p 79; Sutton, "Volumetric Analysis," 10th ed., p 245

[3] THIS JOURNAL, 32, 588 (1910).

[4] The procedure was that recommended by McBride, Bull. Bur. Standards, 8, 611 (1912); THIS JOURNAL, 34, 393 (1912).

[5] Pogg. Ann, Erg, Bd 6, 622 (1874).

was determined. From the data obtained the density of lead oxalate was found to be 5.28. In computing the total excess of reagent from the aliquot titer, the latter was multiplied by the ratio of the true volume of the solution to the actual volume delivered by the pipet.

Inasmuch as the computation of results was troublesome until it was condensed to routine, it is considered advisable to illustrate, by specific instance, the final method used.

Total normal acid added	58 37
Excess of acid, by alkali titration	17 26
Normal acid equivalent to basic lead	41 11

$$PbO = \frac{41\ 11 \times \frac{1}{2} M\ W\ PbO}{Wt\ of\ sample\ (28\ 86\ g\ )} \qquad 15\ 89\%$$

Total $N/3$ oxalate added	400 32
Excess oxalate by permanganate titration	16 36
Oxalate equivalent to total lead	383 96
Ditto in normal solution	127 99
Total lead equivalent minus basic lead equivalent 127 99 −41 11 =	86 88

$$Pb(C_2H_3O_2)_2\ present = \frac{86\ 88 \times \frac{1}{2} M\ W\ Pb(C_2H_3O_2)_2}{Wt\ sample\ (28\ 86)} = \qquad 48\ 95\%$$

The computation from the analysis as sulfate was similar, the total added acid being the sum of the acetic and sulfuric acids.

Synthesis of Basic Acetates.

The usual methods of preparing the basic lead acetates have consisted of boiling the neutral acetate with varying quantities of lead oxide. In the present work the compounds were made by the interaction of the neutral acetate and a suspension of lead hydroxide. These reactions were in many cases very striking and, in contrast to the long period of boiling required in the case of the oxide, they occurred with great rapidity.

A few instances will illustrate the e phenomena:

In the preliminary work before the saturation curves had been located, a synthetic mixture was made up of about the composition 20% PbO and 15% $Pb(C_2H_3O_2)_2$. The hydroxide was added in the form of a suspension in water. On shaking up the mixture there was an immediate solution, with the exception of a slight turbidity. Then after a few minutes the entire solution stiffened to a solid mass. This was due to the crystallization of $Pb(C_2H_3O_2)_2.2PbO.4H_2O$.

Another synthetic mixture was made up of composition 20% PbO, 53% $Pb(C_2H_3O_2)_2$. In order to prepare a mixture containing little enough water it was necessary to dry both the neutral acetate crystals and the hydroxide suspension, the latter to a stiff paste, in a desiccator. On weighing out the components into a bottle the unmixed mass had the appearance of nearly dry solid material. After a few seconds' vigorous shaking

the reaction occurred rapidly and the whole mass was transformed into
a mobile liquid. At the same time there occurred a very considerable
absorption of heat.

The Establishment and the Determination of the Equilibria.

The equilibria were established in long narrow flasks of thin glass
which were agitated in a motor-driven rotating frame under the water

SUMMARY OF DATA

Expt No	Solution		Residue		Solid phase	Density of solution $D_{25/4}$	Refractive index n_D
	PbO	Pb(C₂H₃O₂)₂	PbO	Pb(C₂H₃O₂)₂			
1	—0 27[1]	35 19			Pb(C₂H₃O₂)₂	326	
2	+0 10	35 60			3H₂O	334	1 380
3	1 01	37 14				367	
4	3 38	38 93				422	
5	6 01	41 95	2 85	64 34		531	
6	9 47	44 71				658	
7	14 22	47 88	9 44	60 68			
8	14 44	47 92				1 852	
9	15 89	48 95	14 10	60 99	Transition		1 456
10	15 90	48 42	16 68	58 84	3Pb(C₂H₃O₂)₂	1 930	1 456
11	16 25	48 85	16 63	55 52	PbO	1 942	1 4605
12	16 29	48 87			3H₂O	1 941	
13	16 65	49 04				1 956	
14	18 83	48 71	18 61	58 98		2 024	1 467
15	22 23	48 52	20 50	60 05		2 161	1 4845
16	22 94	48 96	21 72	57 06		2 193	1 491
17	23 28	49 14	21 81	57 05			
18	23 53	49 01				2 220	
19	24 71	49 22	26 02	52 90	Transition	2 282	1 502
20	24 77	49 20	27 44	52 12	Transition	2 279	1 501
21	23 59	43 17			Pb(C₂H₃O₂)₂ 2PbO 4H₂O	2 048	1 469
22	22 78	40 78	29 14	40 39		1 951	
23	19 63	31 40	25 14	32 60		1 657	
24	18 73	29 63				1 599	1 409
25	14 62	20 06	35 00	30 49		1 382	1 379
26	13 41	19 65				1 348	
27	10 66	12 99				1 229	
28	8 47	8 64				1 157	
29.	8 08	8 07					
30	7 84	5 36					
31	7 87	5 27				1 119	
32	7 78	5 25				1 117	1 344
33	7 17	4 71			Pb(OH)₂		
34	6 84	4 31				1 100	1 343
35	6 54	4 25	68 60	1 39		1 095	
36	5 91	3 82				1 085	1 340
37	5 29	3 40				1 075	
38	0 20	0 11					

[1] Acidity expressed in terms of PbO

of a thermostat for at least 48 hours. The temperature of the bath was constant to about 0.01°. All experiments were made at 25.00°. In order to determine with certainty whether equilibrium was reached in 48 hours, the time of agitation in a number of experiments was increased by varying amounts. In these instances practically identical results within the error of experiment were obtained. See Experiments 7 and 8, 11 and 12, 19 and 20, 31 and 32. Moreover, in general, the times of agitation were very varied, never less than 48 hours, frequently as long as seven days. The fact that smooth curves were obtained is further evidence that equilibrium was attained.

After the mixture had reached equilibrium the flask was placed in a rack in the thermostat to permit the solid phase to separate. In taking the sample the solution was drawn up into a pipet and a measured volume delivered into a weighed 500 cc. volumetric flask. The flask and substance were then weighed. This procedure gave the weight of the sample and, as the subsequent treatment was in the same flask, no further transfer of material was necessary. A knowledge of the volume and weight of the solution permitted a calculation of the density. The values to three decimals are given in the summary of data.

In studying the solid phase the indirect method of Schreinemakers[1] was employed. The supernatant solution was decanted and a portion of the solid with the adhering mother liquor shaken into the volumetric flask for analysis.

The Solid Phases.

As a study of the diagram, Fig. 1, will reveal, there are four solid phases which can exist in equilibrium with aqueous solutions of the two solid components.

The neutral lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, consists of brilliant monoclinic prisms. It can exist in equilibrium with an aqueous solution containing dissolved substance of its own composition. It is also capable of existence in equilibrium with solutions containing as much as 15.9% basic lead, estimated as oxide. Its saturation curve is continuous with one extending into acid solutions.

The tetra-lead-monoxy-hexacetate,[2] $3Pb(C_2H_3O_2)_2.PbO.3H_2O$, consists of perfectly formed needles which may attain the length of 5 mm., but usually appear as small, lustrous, silky crystals whose form is difficult to recognize. It is exceedingly soluble in water and forms solutions of density, 1.93 to 2.28. It cannot exist in equilibrium with aqueous solutions of itself, but depends upon an excess of dissolved basic lead.

[1] *Z. physik. Chem.*, 11, 76; Bancroft, *J. Phys. Chem.*, 6, 179; Findlay, "Phase Rule," 3rd ed., p. 305.

[2] For nomenclature see Hoffman, "Dictionary of Inorganic Compounds," Vol. I, p. 44.

On account of the small size and softness of the crystals, and the high density and viscosity of the mother liquor, it is practically impossible to isolate in pure form. It is probable that these experimental difficulties are responsible for the fact that its composition has not previously been correctly ascertained. To establish the formula of this compound six lines were determined. These gave rise to a large number of intersections, of which ten were at sufficiently large angle to be considered representative of the solid phase. The mean of these ten was the accepted value.

Calc. for $3Pb(C_2H_3O_2)_2$ PbO $3H_2O$. $Pb(C_2H_3O_2)_2$, 77 9, H_2O, 4 3, found 77 9 and 4 2

The apparent precision of the accepted value is somewhat deceptive, as the individual determinations are slightly scattering.

The tri-lead-dioxy-diacetate, $Pb(C_2H_3O_2)_2.2PbO.4H_2O$, has been isolated previously and its formula, with respect to the two solid components, correctly ascertained. It has been hitherto described as an amorphous solid and, in fact, as it usually occurs, it has that appearance. Nevertheless, by slow evaporation of its clear solution it can be obtained in small, rather ill-formed, needles which leave no doubt of its crystalline character. Its saturation curve has a very great length, extending from 13% to 74% of dissolved substance. It is stable in contact with aqueous solutions of itself.

Calc for $Pb(C_2H_3O_2)_2$ $2PbO$ $4H_2O$ PbO, 52 9, H_2O, 8 55, found 52 5 and 8 6

Lead hydroxide, $Pb(OH)_2$, is in equilibrium with solutions containing less than 4.8% of lead acetate.

The Quadruple Points.

At 25° there are three sharply defined quadruple points. The transition mixture at B was obtained by approaching it with successive additions of neutral acetate to the solution of the monoxy-acetate.

The transition mixture at C was reached in two separate experiments, one a new synthetic mixture which was filtered and allowed to concentrate in a desiccator, the other a mixture formed by addition of neutral lead acetate to a solution which was on the saturation curve CD. The solutions proved to be of identical composition; while the solid phases, as shown by the arrows, were mixtures in different proportions of the two solid phases in equilibrium with the two intersecting saturation curves.

At the point D, the dioxy-acetate and lead hydroxide can exist in contact with the same solution.

The Saturation Curves.

The saturation curves in equilibrium with the four respective solid phases are in some respects noteworthy. The curve AB, representing the solubility of neutral lead acetate in basic solutions, shows a remarkably

high rate of increase of solubility of the solid phase. In order to cause such a rise in solubility there must occur a more deep-seated change in the solution than the mere admixture of two solutes. The curve is slightly convex toward the solid phase. The curve BC is approximately a straight line. The solution contains a nearly constant quantity of lead acetate with varying lead oxide content. Since the dioxy-acetate has a low temperature coefficient of solubility and the neutral acetate a high one it is conceivable that at some temperature in the neighborhood of 0° this
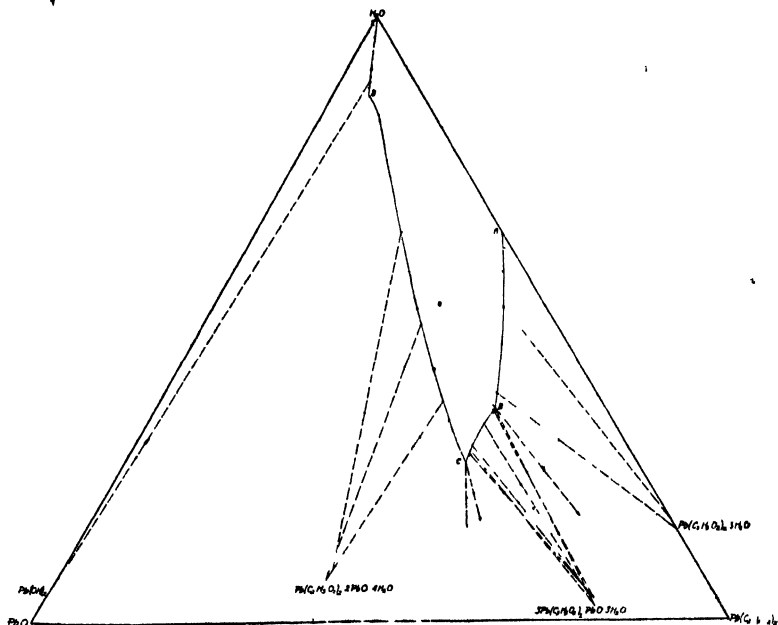
Fig. 1.—Isothermal equilibrium at 25°. The curves AB, BC, CD and DE represent the composition of the solution in equilibrium with the respective solid phases The area ABCDE encloses the region of unsaturated solutions Note the great increase of solubility of the neutral acetate in basic solutions the high solubility and limited range of stability of the monoxy-acetate, and the very great range of stability of the dioxy-acetate. The data are computed with respect to weight per cent.

small curve would be squeezed out of existence. At such temperature we should have three solid phases in equilibrium with the same solution and vapor and hence a nonvariant point. The curve CD in equilibrium with the dioxy-acetate shows again the great effect upon the solubility which a relatively slight change in the ratio of basic to neutral lead exerts. It is slightly concave toward the solid phase. The curve DE is practically linear.

The plot, Fig. 1, was constructed with reference only to weight percentages. If the data are plotted in molecular percentages, a diagram of the same general form results, but of very much diminished area. On account of the high molecular weight of the lead compounds the molecular percentages become very low.

A study of the purely chemical equilibria enables us to understand some of the changes which occur in the solution and thus to predict, in some measure, the course of the saturation curves.

Starting at the point A of the diagram, we find neutral lead acetate crystals in equilibrium with a solution of neutral lead acetate. We may suppose that the first equilibrium is between whole molecules thus:

$$\text{solid} \qquad\qquad \text{molecules in solution}$$
$$(1)\quad Pb(C_2H_3O_2)_2 \quad \rightleftharpoons \quad Pb(C_2H_3O_2)_2$$
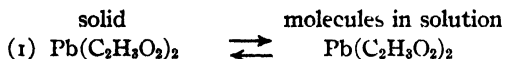
neglecting the water of hydration.

Undoubtedly the dissolved salt is then to some extent both ionized and hydrolyzed. However, it must be equilibrium (1) which determines the solubility of the crystals and the constant of that equilibrium must be maintained whatever subsequent reactions occur.[1]

Upon addition of lead hydroxide the first basic acetate which makes its appearance has the formula $3Pb(C_2H_3O_2)_2.PbO.3H_2O$. The solution does not become saturated with respect to the solid phase until about 15% of lead oxide is dissolved. Here again, an equilibrium between whole molecules of solid and dissolved basic acetate must exist. The solution represented by the saturation curve AB of the neutral acetate must also contain this same molecular species although in a state of unsaturation. There must then be in the solution an equilibrium between the dissolved molecules of neutral acetate and those of the monoxy-acetate thus·

$$(2)\quad 3Pb(C_2H_3O_2)_2 + PbO \rightleftharpoons [Pb(C_2H_3O_2)_2]_3.PbO$$
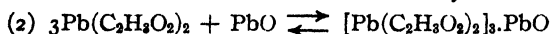
Now from this equation it appears that one molecule of lead hydroxide causes the disappearance of three molecules of neutral acetate. The equation would occur almost totally from left to right at the low concentrations of the basic acetate. If then we add lead hydroxide to a saturated solution of the neutral acetate we cause a disproportionately large quantity of dissolved lead acetate molecules to disappear. But now the original equilibrium between the neutral crystals and the dissolved neutral molecules must be maintained, hence a large quantity of neutral acetate must go into solution. This would account for the astonishing increase of solubility of the neutral acetate in basic solutions.

Of interest in this connection is the correlation of another phenomenon. Parsons[2] has shown that the freezing point of a lead acetate solution is

[1] This must be rigorously true for minute changes in the solution

[2] J Phys. Chem , 11, 659 (1907).

raised by the addition of basic lead even although more solid substance is in solution. In his discussion he very justly pointed out that no evidence of a molecular complex then existed. If, however, Equation 2 is substantially correct the addition of one molecule of lead hydroxide to three of acetate has caused the formation of but one molecule of the basic compound or a disappearance of three molecules. Since the lowering of freezing point depends only upon the number of dissolved particles, we should expect a rise and not a lowering upon the addition of basic lead.

If we make the assumption that the constancy of equilibrium (1) is rigidly maintained throughout the wide variation of conditions represented by the curve AB, we can make a further prediction in regard to the saturation curve. If we continue the addition of lead hydroxide, the concentration of the basic acetate continually increases and gradually Equation 2 becomes important in the sense from right to left Thus at the farther end of the curve the addition of a small quantity of lead hydroxide must produce a smaller relative effect than at the low concentrations In other words, the saturation curve should have, according to this theory, the convex shape which was found by experiment

The nature of the solution represented by AB undergoes some variation between A and B in respect to basicity, viscosity, and density, and it seems at first somewhat violent to assume the constancy of Equation 1 On the other hand, if we calculate in molecular per cent instead of weight per cent. we find that the point A corresponds to but 2 98% lead acetate and the point B to 6 93% lead acetate and 3 28% lead oxide. As far as molecular percentages are concerned, we are still dealing with fairly dilute solutions This justifies, to some extent, our assumption.

The mechanism of the reaction cannot be supposed to be as simple as represented by Equation 2, but even so, we may say with certainty that the end members of the chain of reactions are just as represented, namely, neutral lead acetate molecules and basic lead acetate molecules, and whatever reasoning has been applied would be equally valid if the mechanism of the reaction included the products of ionization and hydrolysis

With regard to the second saturation curve BC, viz, that in equilibrium with the solid phase $[Pb(C_2H_3O_2)_2]_3.PbO$, let us suppose that we are following the curve from right to left. Neutral lead acetate has now acquired so great a solubility that the basic acetate is the more insoluble substance and separates from its own saturated solution As we continue to add lead hydroxide the following reaction becomes important

$$(3) \quad [Pb(C_2H_3O_2)_2]_3.PbO + 5PbO \rightleftarrows 3[Pb(C_2H_3O_2)_2 2PbO]$$
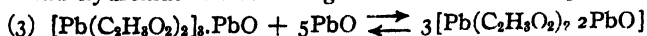
Here it requires five molecules of lead hydroxide to cause the disappearance of one molecule of the monoxy-acetate and we should expect just

what happens experimentally—a much slower increase of solubility of the solid phase with continued addition of lead hydroxide. Furthermore, since the dioxy-acetate is a relatively insoluble substance it must reach its saturation after a relatively small addition of lead hydroxide. As we pass down the saturation curve BC of the solid phase $3Pb(C_2H_3O_2)_2.$-PbO we gradually increase the concentration of the dioxy-acetate, namely, $Pb(C_2H_3O_2)_2.2PbO$, until at the quadruple point C we increase it to its saturation point and it begins to separate. Further addition of lead hydroxide converts the soluble monoxy-acetate into the relatively insoluble dioxy-acetate which immediately precipitates. Hence occurs the very rapid decrease of solubility as shown by the saturation curve CD.

The convexity of the curve CD may be explained if we make assumptions similar to those made with the curve AB. Let us start with the transition point D and approach C. This can be accomplished by adding neutral lead acetate to the saturated solution of the dibasic acetate. The reaction is then

(4) $Pb(C_2H_3O_2)_2.2PbO + 5Pb(C_2H_3O_2)_2 \rightleftarrows 2[(Pb(C_2H_3O_2)_2)_3.PbO]$.

The increase of solubility would, according to our theory, depend upon the disappearance of the dissolved dioxy-acetate and the appearance of the very soluble monoxy-acetate. At first the concentration of the monoxy-acetate is low and the reaction proceeds almost entirely in the sense of the equation from left to right. As the concentration of monoxy-acetate increases the former reaction is opposed by the reverse equation and consequently the rate of increase of solubility diminishes. Thus the convexity toward the solid phase.

The slope of the saturation curve DE of lead hydroxide possesses some interest. Upon adding lead acetate the following reaction occurs:

(5) $2Pb(OH)_2 + Pb(C_2H_3O_2)_2 \rightleftarrows Pb(C_2H_3O_2)_2.2PbO + 2H_2O$
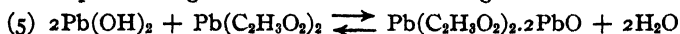
Since, with lead hydroxide as the solid phase, we are far from the region of stability of the neutral acetate, the latter cannot remain in considerable concentration, and since the hydroxide itself has but slight solubility, we should expect the dissolved substance to consist almost entirely of the dioxy-acetate. In this compound the weight ratio of lead acetate to lead oxide is 0 73 while in the solution of the curve DE it is 0 64. This indicates a slight excess of dissolved lead hydroxide which apparently acquires an increased solubility in solutions of basic acetates.

If this latter conclusion is correct, reaction (5) will continue in the sense from left to right even after the point D has been passed and the solid phase has changed from the hydroxide to the dioxy-acetate. During the initial stages of the curve DC the addition of neutral acetate results only in an exhaustion of this dissolved hydroxide and makes no demands upon the dioxy-acetate. Consequently reaction (4) does not become predomi-

nant until lead hydroxide is exhausted.   As a result of this we find at the upper end of CD a slight but unmistakable change of curvature

In conclusion, it is a pleasure to acknowledge the kind assistance rendered by Dr William Blum, of this Bureau, who made many valuable suggestions in regard to analytical procedure, and by Dr John Johnston, who read the manuscript critically

Summary.

1   The analysis of basic lead acetate was performed by measuring the volume of standard acid neutralized by the basic lead and the volume of reagent required for the complete precipitation of lead

2   The synthesis of the basic acetates was accomplished by the interaction of lead acetate and lead hydroxide   Some of the accompanying phenomena are described

3   A theory of the course of the saturation curves is proposed

4   The solid phases capable of existence are

$Pb(C_2H_3O_2)_2$ $3H_2O$, brilliant monoclinic crystals   It can exist in equilibrium with acid and neutral solutions and with basic solutions containing as much as 15 9% lead oxide   Its solubility in water is 35 50%

$3Pb(C_2H_3O_2)_2 PbO 3H_2O$ crystallizes in needles   It is exceedingly soluble in water and forms solutions of density 1 93 to 2 28   The substance is unstable in contact with solutions of itself   For its existence in equilibrium with a solution there must be an excess of dissolved basic lead   The solutions contain at the extremes of the saturation curve 15 89% PbO, 48 95% $Pb(C_2H_3O_2)_2$ and 24 74% PbO, 49 21% $Pb(C_2H_3O_2)_2$. $Pb(C_2H_3O_2)_2 2PbO 4H_2O$ consists of needles which may be so small as to seem amorphous   It is capable of existence in equilibrium with solutions of itself but under such conditions has a solubility of but 13 3% Its saturation curve possesses a very great length   The extremes of solubility are 7 4% PbO, 4 8% $Pb(C_2H_3O_2)_2$ and 24 74% PbO, 49 21% $Pb(C_2H_3O_2)_2$

$Pb(OH)_2$ is stable in equilibrium with solutions containing as much as 7 4% PbO and 4 8% $Pb(C_2H_3O_2)_2$

BUREAU OF STANDARDS,
WASHINGTON D C

ON THE RHYTHMICAL PRECIPITATION OF FERROUS FERRICYANIDE AND FERROUS HYDROXIDE IN JELLY.

BY HENRY JERMAIN MAUDE CREIGHTON
Received September 23 1914

When a drop of silver nitrate solution is placed on a thin layer of gelatin containing potassium dichromate, silver chromate precipitates out in circles which are concentric to the drop of silver nitrate   Such precipitation of silver chromate has been investigated during the past few years.

by Liesegang and others.[1] Analogous phenomena have been observed by Liesegang[2] with mercurous chromate, lead chromate and Prussian blue, and by Morse and Pierce[3] with lead sulfate, silver carbonate, phosphate, bromide and thiocyanate, cobalt hydroxide, barium chromate and mercurous bromide. This phenomenon of rhythmical precipitation is explained by Ostwald's theory of supersaturation.[4]

Phenomena similar to the foregoing have recently been observed by the writer with Turnbull's blue and ferrous hydroxide.

The horizontal part of a glass tube 70 cm. long and 2 cm. in diameter, the ends of which were bent up at right angles, was filled with a 10% solution of agar-agar containing small quantities of potassium ferricyanide and sodium chloride. After the jelly had solidified, the vertical arms of the tube were filled with a dilute solution of sodium chloride, and an iron electrode, made from a clean wire nail, was placed in the liquid in each arm. An electric current having a potential gradient of 0.00679 volt per cm. was then passed through the jelly.

Within a short time after the current was started, the end of the jelly near the anode became blue, and for four days the blue color continued to advance through the jelly. During the following twenty-four hours there was no perceptible advance of the color, but at the end of this time
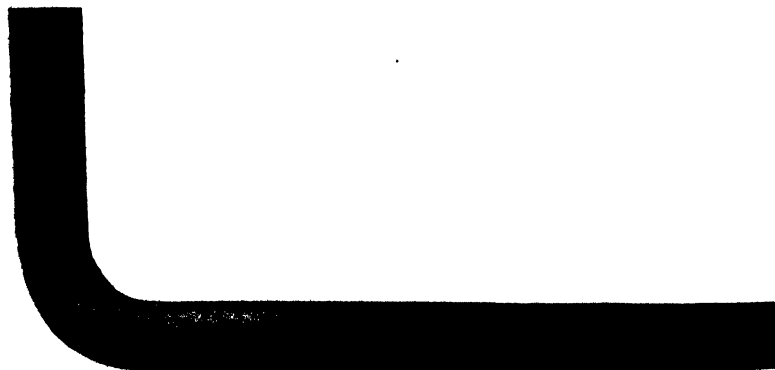
Fig. 1.

a very thin dark blue layer or disc was observed to have formed in the jelly at right angles to the axis of the tube. This blue disc gradually increased in thickness during the next few hours until it attained a width of 1 mm. This disc, which was more intense in color than the blue jelly

[1] R. E. Liesegang, Z. physik. Chem., 23, 365 (1897); 59, 444 (1907); 88, 1 (1914); Morse and Pierce, Ibid., 45, 589 (1903); Bechhold, H., Ibid., 52, 185 (1905).

[2] "Chemische Reaktionen in Gallerten," Düsseldorf, 1898.

[3] Loc. cit.

[4] "Lehrb. d. allgem. Chemie," 2 Aufl., 2, 778.

behind it, was separated from the latter by 3 mm. of practically colorless jelly. At the end of another twenty-four hours a second disc had formed which was separated from the first by 4 mm. of colorless jelly. In this experiment a new disc appeared every twenty-four hours, the discs forming in the direction of the flow of the electric current. The time at which each disc appeared, and the distance between each disc and the preceding one is shown in Table I.

TABLE I.

Number of disc	Turnbull's blue discs		Ferrous hydroxide discs.	
	Time of appearance of disc Days	Distance between consecutive discs Mm	Time of appearance of discs Days	Distance between consecutive discs. Mm
1	0		0	
2	1	4 0	1	3
3	2	4 0	2	5
4	3	5 0	3	3
5	4	4 0	4	5
6	5	3 5	5	4
7			6	4
8			9	6
9			11	4
10			14	6

An experiment similar to the foregoing was carried out, except that the jelly contained small quantities of sodium chloride and phenolphthalein. The ferrous ions diffused into the jelly under the influence of an electric current having a potential gradient of 0.0093 volt per cm. The progress of the hydroxyl ions was followed by means of the phenolphthalein. The ferrous and hydroxyl ions, which were moving in opposite directions, met at the end of one hundred and fifteen days from the beginning of the experiment, and a dark green layer or disc of ferrous hydroxide was precipitated in the jelly at right angles to the axis of the tube. At the end of twenty-four hours, a second disc was observed to have formed. This was separated from the first by 3 mm. of jelly, colored pink by the phenolphthalein. Every day or two a new disc formed, each being separated from the preceding by several millimeters of pink jelly. The discs formed in the opposite direction to the flow of the electric current. The time at which each disc appeared, and the distance between each and the preceding one is shown in Table I. Fig. 1 shows a photograph of the ferrous hydroxide discs. The ferrous hydroxide discs always commenced to form at the bottom of the tube and continued to grow towards the top, always sloping in the opposite direction to the flow of the electric current. Sometimes a new disc started to form before the preceding one was completed. In such cases the old disc ceased growing. The photograph shows several of these partially formed discs.

The cause of the rhythmical precipitation of Turnbull's blue and fer-

rous hydroxide may doubtless be ascribed to supersaturation phenomena. As the Fe^{++} ions are carried into the jelly by the electric current, a metastable supersaturated solution with respect to Turnbull's blue first forms. Ultimately precipitation occurs and the $FeCy_6^{---}$ ions in the neighborhood are removed; the Fe^{++} ions then advance a few millimeters and form a new supersaturated solution, when the process is repeated. In the case of ferrous hydroxide, the OH^- ions form a supersaturated solution with the Fe^{++} ions. After precipitation has taken place, the OH^- ions must advance a few millimeters before a sufficient number of Fe^{++} ions are encountered to form a new supersaturated solution.

CHEMICAL LABORATORY, SWARTHMORE COLLEGE,
SWARTHMORE, PA

THE SULFATE METHOD FOR STANDARDIZING A MAGNESIUM SALT SOLUTION.

BY C W FOULK AND O R SWEENEY

For a number of years one of us has had work in progress on the precipitation of magnesium as magnesium ammonium phosphate, the object being to discover, if possible, the causes of the discrepancies among the results by different methods and especially those obtained by various workers with the same method. As the investigation progressed it seemed to fall more and more into a study of the preparation of pure material and of the art of measuring the substances produced, until finally it narrowed to the question of preparing and standardizing a solution of a magnesium salt.

This trend of the work was an evolution rather than a part of the original program. At first a large amount of work was done in the way of comparing methods and of course different results were obtained. Different results were also obtained at times by the use of the same method. These differences were small and might have been due to impure reagents, improper handling or finally to lack of knowledge as to the exact concentration of the solution of magnesium salt used. As the subject was taken up by successive advanced students whose interest prompted them to undertake a share in the experimental work, new sources of error were found and studied. When these corrections were applied, they sometimes had the effect of reducing or eliminating the discrepancies in the results of the magnesium-ammonium-phosphate precipitations and sometimes they had the effect of making these discrepancies larger. The notes on the earlier part of this work were destroyed by the burning of the Chemical Building at the Ohio State University in 1904. A summary of the rest will be presented in a separate paper.

The lack of agreement in our results could, of course, be due to one, or to a combination of several causes, but the question of our knowledge of the content of the magnesium salt solution used seemed to be the most fundamental. Unless we could be absolutely sure of that, within our experimental errors, looking for other causes seemed a doubtful quest.

In the previous work the general plan had been to prepare pure magnesium chloride and then to standardize the solutions made from this pure chloride by treating a measured portion with a slight excess of sulfuric acid, evaporating and igniting the residue under carefully regulated conditions. This method appears to have the best standing in the literature, though it is not universally accepted.[1]

It gave beautifully concordant results, it is true, but that meant only that it *might* be right. Other methods also gave concordant results, but they differed from the $MgSO_4$ values. Which was right, was the question we wanted answered and our preliminary problem was to find a way to do it. It is not easy to test a method of measurement unless a more accurate method is at hand and it at once became evident that we must look beyond the range of the usual analytical procedures to find such a method for the magnesium salt solutions.

In the preparation of the pure magnesium chloride, methods that had been used by atomic weight workers had been adapted, that is, we used the same purification processes but did not carry them quite so far. For example, recrystallizations were made only three or four times instead of nine or ten times. It seemed worth while, then. to see if more of the methods of atomic weight determinations might not be adapted to a problem of this sort.

Richards and Parker,[2] in the determination of the atomic weight of magnesium, had used anhydrous magnesium chloride as the starting point. This was sufficient to give that substance ample standing as an ultimate magnesium material if only the experimental difficulties of handling it could be overcome. It had the further advantage of being the very salt of which our standard solutions were composed, so that if we succeeded in preparing the chloride and in quantitatively transforming it into the sulfate it would be at least strong evidence of the correctness of the sulfate method of standardization. Accordingly, this was the plan of work finally adopted, the details of which will now be given.

Preparation of Material.

Distilled Water.—The distilled water of the Ohio laboratory is prepared by boiling the ordinary tap water by means of a steam coil and condensing the steam thus formed in block tin, the water then being stored in a tinned copper tank. The original tap water is softened by the city water works.

[1] Bube, *Z. anal. Chem.*, **49**, 535 (1910).
[2] *Z. anorg. Chem.*, **13**, 81 (1897).

with lime and soda ash and is then filtered through mechanical filters. This furnishes a high grade tap water containing little organic matter and carbon dioxide. The water used in this investigation was made by redistilling the ordinary distilled water from a Jena glass flask after the addition of a little sulfuric acid and of potassium permanganate. The condenser was block tin, a wad of glass wool being used to prevent the carrying over of spray from the boiling. Only the middle portions of the water were collected. It was received and stored in "Resistenz" glass bottles which had been steamed out.

Hydrochloric Acid.—This was prepared by dropping c. p. sulfuric acid into c. p. hydrochloric acid solution, sp. gr. 1.20, and receiving the evolved HCl in distilled water in a platinum dish which was set in a large glass vessel covered by a glass lid, provided with a tubulure for admitting the tube carrying the HCl gas. The evolution flask was arranged with a two-holed paraffin-soaked cork carrying a separatory funnel and the egress tube. No heat was applied.

Ammonium Hydroxide.—The so-called c. p. ammonium hydroxide solution (0.90 sp. gr.) was heated in a Jena flask and the NH_3 conducted through a Jena glass tube into water contained in a platinum dish which was protected from dust as described under the preparation of hydrochloric acid. A rubber stopper was used.

Ammonium Chloride.—Various attempts to purify ammonium chloride by sublimation proved and finally the scheme illustrated in Fig. 1 was used. Hydrochloric acid gas, generated in A, and NH_3 from B were passed into water in the platinum dish C till NH_4Cl began to crystallize out. The saturated solution was then analyzed, and the volume required in the preparation of the double chloride of ammonium and magnesium was calculated. This preparation left no residue on ignition.

Carbon Dioxide.—This was generated in a Kipp apparatus by the action of c. p. hydrochloric
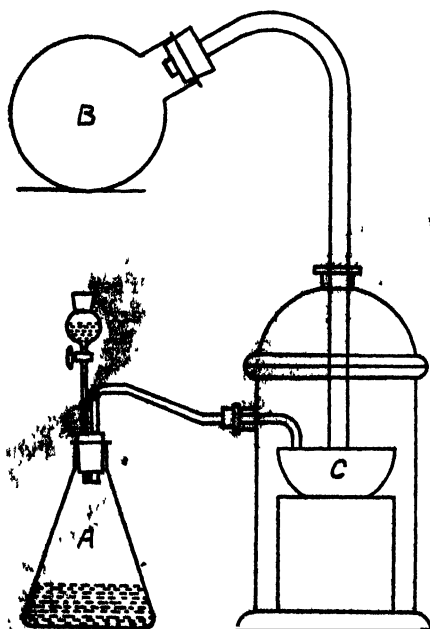
Fig. 1.

acid on marble. It was washed by passing it through $KMnO_4$ solution, water and sulfuric acid.

General Precautions and Tests of Purity.—All glass ware used was either of the Jena or Resistenz brand, and in all cases the vessels were steamed for an hour before using. In order to keep out dust, the reactions, if possible, were made to take place in covered vessels provided with tubulures for admitting the reagents. When this could not be managed, the substances were protected by dust shields or by watch glasses. Where the details of the method are not given below, it can be assumed that due precautions were taken. Ignitions were made with an alcohol lamp.

The different salts, acids, ammonia and water used were all tested with the spectroscope and if a sodium line showed they were rejected. Since all the materials originally contained a little sodium it was assumed that the purification had been carried far enough for our purposes when the sodium was eliminated.

Magnesium Salt.— The contents of an unopened bottle of c. p. $MgCl_2.$-$6H_2O$, containing 600 g. of the salt, were dissolved in 500 cc. of redistilled water. Apparently this was an unusually good specimen of the salt. Treatment with H_2S and a little NH_4OH produced no precipitate and also no test for calcium could be found with $(NH_4)_2C_2O_4$. Duplicate tests were made on portions of the solution to which very small quantities of the heavy metals and of calcium had been added and these portions at once gave positive tests with H_2S and with $(NH_4)_2C_2O_4$. The spectroscope, however, showed the presence of sodium. To effect the separation from this metal, precipitation of the magnesium as the double carbonate of magnesium and ammonium was employed.[1]

A number of experiments were first made to determine the best conditions for precipitation and finally the following was adopted: About 25 cc. of the concentrated magnesium chloride solution were placed in the platinum dish A, Fig. 2, and diluted till the dish was nearly full. Ammonia produced in the still B, and carbon dioxide, made and washed as described above, were now led into the solution as shown in the figure. Cold water was kept circulating around the dish by means of the tubes shown at H. Both the NH_3 and CO_2 were passed into the solution for two hours when the NH_3 was stopped and the current of CO_2 allowed to continue for twenty minutes more. This caused the precipitate to take on a crystalline form, that made it easy to handle. The dish was finally removed from its container and the salt washed 40 to 50 times by decantation. The precipitate was then transferred to a platinum funnel, containing a finely perforated platinum cone, on which it was washed for about four hours, after which it was transferred to a platinum dish, covered with a watch glass, and heated in a hot air oven till no more odor

[1] Bray, THIS JOURNAL, **31,** 611 (1909).

of ammonia could be noted. The salt so obtained was labeled Preparation I.

The spectroscope showed no sodium, and quantitative tests for calcium and platinum gave negative results. This procedure of treating 25 cc. portions of the original magnesium chloride solution was repeated until a sufficient amount of Preparation I was obtained.

Preparation II was next made by dissolving portions of No. I in HCl, in the large platinum dish in the apparatus used before, and precipitating and washing as described above for Preparation I. This salt was also tested spectroscopically and showed no sodium.

Double Chloride of Ammonium and Magnesium.—A suitable amount of Preparation II was placed in a large platinum dish, covered with water and hydrochloric acid gas passed in till the salt was dissolved. Ammonium chloride in slight excess of the amount to make $MgCl-NH_4Cl$ wasthen added. (The approximate amount of magnesium in Preparation II had been determined.) The mixture in the dish was evaporated just to dryness over an alcohol lamp, after which the resulting mass was dissolved in water and crystallized. The first crop of crystals was again dissolved and recrystallized. The product so obtained was preserved and marked Preparation III. All reagents used in preparing it were the pure ones described above and all the operations were carried out in platinum. The greatest precautions against dust were also observed.
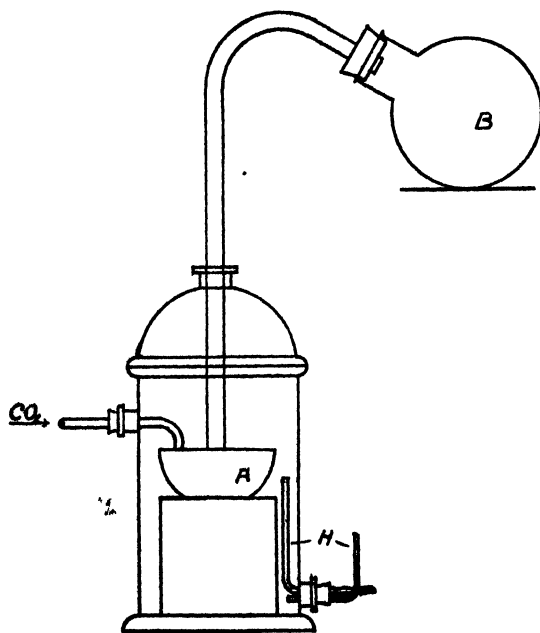
Fig 2.

A number of portions were discarded, because, during the evaporations, a scum gathered on the surface of the solution. The nature of this scum was not learned, further than that it was completely volatile.

Apparatus for the Preparation of Anhydrous Magnesium Chloride and its Conversion into Magnesium Sulfate.

Magnesium ammonium chloride, when heated in a current of dry hydrochloric acid gas, loses water and ammonium chloride and leaves a residue of magnesium chloride which can be fused in order to free it from the last traces of volatile matter. The anhydrous magnesium chloride is, however, so hygroscopic that it must, at all times, be protected from the least trace of moisture. Richards and Parker,[1] in their determination of the ratio $2Ag : MgCl_2$, used the well-known Richards apparatus, which permitted the bottling of the boat containing the magnesium chloride before it was exposed to the air of the laboratory. Such an apparatus with its specially ground glass connections was, however, not available for us and we therefore were obliged to find a substitute, the details of which can be seen from Fig. 3. It is perhaps needless to say that this
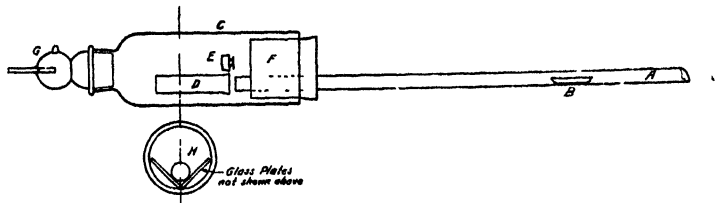
Fig. 3.

apparatus, crude as it may be, was the result of much experimenting before a workable combination was obtained. Its operation was as follows:

The hollow, ground-glass stopper G was removed and the platinum boat containing a portion of the double chloride was pushed into place in the combustion tube A, which was supported in a long combustion furnace. The weighing bottle D and its stopper E were next put into the bottling chamber C, which was then closed by the stopper G. Dry HCl was next passed into the apparatus through the tube sealed into the stopper G, the combustion tube was heated to the requisite temperature, the HCl was displaced by dry air and when the whole had cooled down to the temperature of the laboratory, the boat was pushed back into the weighing bottle by means of a long glass rod operated from the other end of the combustion tube. The stopper was likewise pushed into the weighing bottle, after which the bottling chamber was opened by removing G and the weighing bottle taken out to the balance.

In the construction of this apparatus the difficulty that seemed hardest to overcome was the matter of the connection between the combustion tube and the bottling chamber. In the Richards apparatus, which was our model, this was effected by a ground-glass joint. It served the

[1] *Loc. cit.*

two necessary purposes of giving a tight connection and yet making disconnecting easy for inserting the weighing bottle. We had, however, no means for grinding such joints and therefore had to meet the situation in some other way. Experiments showed that dry HCl acted upon rubber stoppers, but appeared to have no effect upon paraffin. A paraffined cork therefore suggested itself. The two important objections, the low melting point of paraffin and the nuisance of melting in the joint for each determination, were overcome (1), by using a very long combustion tube so that the joint did not come near the furnace, and (2), by having the opening into the bottling chamber at the other end.

This permitted the use of any suitable piece of stock apparatus already provided with a ground stopper carrying a sealed-in tube for connection with the HCl generator and air supply. Such a stock piece was found in the ordinary gas washing bottle. One about 24 cm. long and 6 cm. in diameter was taken, the bottom was cut off for the insertion of the cork with the combustion tube and one of the tubes through the stopper was closed, the other serving for the connection with the drying train. This made an excellent bottling chamber and permitted a permanent connection with the combustion tube. This was accomplished by using a cylindrical cork F, so that it could be inserted its full length into the bottling chamber. This cork, after being bored, was dipped into melted paraffin, the combustion tube was then inserted and the cork pushed into place. The apparatus was then supported in an upright position and melted paraffin was poured through a funnel onto the cork till a thick layer was produced, the end of the combustion tube being left almost flush to avoid the pocketing of gas behind it. This gave a strong joint that withstood perfectly the handling it received. Owing to the length of the combustion tube and protection shields of asbestos board, not the least softening occurred. It was not called upon to withstand pressure and consequently remained tight. The most careful watching failed to show any action of the HCl gas upon the paraffin or any penetration of the gas to the cork under the paraffin.

The handling of the stopper of the weighing bottle was facilitated by the construction of a trough from two narrow glass plates in the bottom of the bottling chamber, a cross-section of which is shown at H. The cork F had an eccentric boring so that the end of the combustion tube came opposite the opening of the weighing bottle as it lay in the trough. The bottling chamber was long enough so that, after the boat had been pushed into the weighing bottle by means of a long rod inserted from the other end, the bottle itself could be pushed back a little to allow the stopper previously placed on it to fall down in front of the mouth, from which position it was easily pushed into place and could be tightened by light blows with the end of the rod.

The apparatus for generating and drying the HCl gas and for drying the air is illustrated in Fig. 4. A, A, A, A are gas washing bottles. These were half filled with concentrated sulfuric acid. The bottle B was of
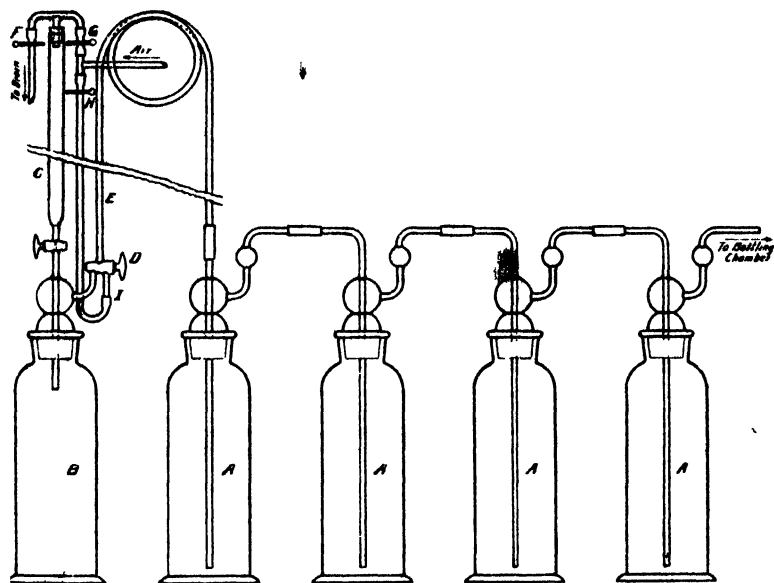
Fig. 4

the same size and design. The large tube C and the two-way cock D and tube E were sealed to the tubes through the stopper. Hydrochloric acid gas was generated by dropping concentrated sulfuric acid from the buret C into concentrated hydrochloric acid solution in B.

On first trying this apparatus it was found that the back pressure was so strong that the HCl gas was forced up through the column of H_2SO_4 in the buret. To prevent this, the arrangement of T-tubes and rubber tubing, as shown in the drawing, was put on. This was connected to the air supply of the laboratory, the pressure of which, for our purposes, was regulated by inserting a T-tube dipping into a mercury well as shown in Fig. 5. The supply of air was kept at such a point that a slow stream of bubbles constantly escaped through the mercury. By closing F and setting the two-way cock D so that an opening from B to A was provided, and leaving G open, an air pressure of any desired amount, as controlled by the regulator above, could be maintained over the acid in C When

Fig. 5

the stream of hydrochloric acid was to be replaced by air, the two-way cock was turned so as to disconnect B and connect the tube E with the tube I. By closing G and opening H a current of air could be sent through the washing bottles. By opening F any HCl gas still coming from B could escape through C to the drain.

The washing bottles themselves were connected by joints made from Kotinsky's cement, as shown in Fig. 6. A and B are the glass outlet

Fig. 6.

and inlet tubes, respectively, of two bottles. C is a short piece of glass tubing, large enough to slip loosely over the other two. The space between was filled with the Kotinsky cement.[1] This arrangement made a very strong and satisfactory joint.

The suction and absorption flask illustrated in Fig. 7 was employed for disposing of the fumes from the treatment of the double chloride and it also served, it is believed, to prevent a back current of laboratory air into the main apparatus. The tube A fitted loosely over the end of the combustion tube, so that when suction was applied at B a steady current of air flowed through the space between the two tubes carrying the ammonium chloride and hydrochloric acid into the sodium hydroxide solution. This arrangement was preferred to a direct connection with the combustion tube, because it did not produce
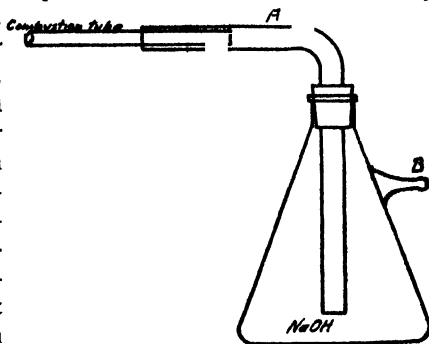
Fig. 7.

reduced pressure in the apparatus with consequent danger of moist air leaking in and because it was easily handled and did not clog with solid ammonium chloride. As a final point in the construction of the apparatus it should be mentioned that the ground-glass joint of the bottling chamber and the two glass cocks on the HCl generator were lubricated with syrupy phosphoric acid.

Weights and Balance.—The weights used were gold plated, from Sartorius. They had been calibrated by the Bureau of Standards and were marked N-5543. The balance was a long arm Troemner. Dishes of sulfuric acid were kept inside the case.

Method of Weighing.—All weighings were made by the method of tares. The magnesium chloride and the magnesium sulfate, excepting

[1] THIS JOURNAL, **30**, 13 (1908).

where the crucible method (see below) was used, were in a platinum boat which was contained in a glass-stoppered weighing bottle. Another bottle of similar size and shape was tared against this one in such a way that it was a trifle lighter than the first one plus the empty platinum boat.

In the crucible method for the conversion of the chloride into the sulfate the same method of weighing was used. The crucible containing the sulfate was put into a short, wide-mouthed weighing bottle, which was counterpoised by another one of the same size and shape carrying an empty crucible.

In all cases after removing the weighing bottle from the combustion apparatus it was placed, together with its tare, in a desiccator over sulfuric acid and left for several hours. On being taken out for weighing, the glass pieces were wiped with a dry cloth and left on the balance for about an hour. When the empty boat was weighed, it was first heated to glowing and placed at the side of its weighing bottle in the desiccator to cool. When cool the desiccator was opened, the boat put into the bottle and the stopper inserted. This operation required only a few seconds. A similar procedure was employed in obtaining the weight of the empty crucible for the sulfate method.

Typical Operations.

(1) *Conversion of the Double Chloride into Anhydrous Chloride.*—The platinum boat, previously weighed, was filled with Preparation III and placed in the combustion tube about three-fourths of the length of the tube distant from the bottling chamber. The weighing tube with its stopper was next placed in position in the bottling chamber which was then closed. The absorption apparatus at the other end of the tube was now put into place and the suction started. A current of dry HCl was passed through the apparatus and continued till all the air was displaced, when two low flames were started at a distance from the boat so that the current of HCl was warmed. This was continued until the water was driven out of the salt, a point easily recognized by experience. More burners were then lighted in such a series that the heat was very gradually increased. When the ammonium chloride was all expelled, burners were lighted along the full length of the tube so as to obtain the maximum temperature around the boat for the purpose of fusing the $MgCl_2$. Occasionally an extra Bunsen burner was necessary to accomplish this. The chloride was kept in a molten state for about ten minutes, after which it was gradually cooled by turning off a few burners at a time. When cool, the current of HCl was replaced by one of dry air, which was continued till all of the HCl was driven out. The absorption apparatus was then removed and the boat pushed back into the weighing tube by means of a long rod. The stopper was next pushed into place

and tapped fast. The current of air was then shut off and the bottling chamber opened for removing the weighing tube.

(2) *Conversion of the Chloride into the Sulfate.*—Two methods were employed which may be designated as (*a*), the boat method, and (*b*), the crucible method.

(*a*) *The Boat Method.*—The anhydrous magnesium chloride in the boat was covered with dilute sulfuric acid containing o.16 g. H_2SO_4 per cubic centimeter. The excess of water was evaporated on a steam plate—a cast iron box through which live steam circulated—in an apparatus as shown in Fig. 8.

The boat B was placed in a large glass tube A which was laid on the steam box C. A current of air, washed with sulfuric acid and filtered through a wad of glass wool, was passed through the tube A to

Fig. 8.

hasten the evaporation and also to protect the contents of the boat from dust. When the bulk of the water had been removed in this way the boat was placed in the combustion apparatus, the excess of H_2SO_4 driven off and the resulting $MgSO_4$ ignited to constant weight at a low red heat. It was then bottled and weighed as described above for $MgCl_2$.

Trouble was at first experienced during the evaporation of the dilute acid by a tendency of the magnesium sulfate to creep over the sides of the boat. This was remedied by smearing the edges with a trace of vaseline. Blanks were run to prove that no residue was left by the vaseline.

(*b*) *The Crucible Method.*—This consisted in dissolving the chloride and transferring it to a platinum crucible before transforming it into the sulfate. The method was used merely because it more nearly resembled the conditions that would obtain in the actual standardization of a magnesium chloride solution. By way of preparation for this method, the end of the combustion tube was raised slightly while the chloride was in a molten state, thus causing it to collect in one end of the boat, where it was allowed to solidify. Melted magnesium chloride does not wet platinum; consequently, this operation was very successful. The transfer to the crucible was made by putting the end of the boat containing the chloride into the crucible, where it was covered with a little dilute sulfuric acid. After solution was complete the boat was rinsed off, dried and examined for traces of salt that might remain. This manipulation seems more difficult than it really was, for it was possible to remove all the chloride from the boat without filling the 30 cc. crucible more than half full.

The excess of water was driven off by heating on the steam box under the protection of an inverted funnel, the bell of which had upturned edges for collecting the condensation. A current of air, filtered and washed

as described above, was passed through the funnel during the evaporation. The excess of acid was driven off by heating in a small porcelain drying oven. The final ignition of the sulfate was made by setting the crucible on a small platinum triangle in a larger crucible also of platinum. The outer crucible was heated so that the temperature between the two was 700°, as measured by a Hoskin's pyrometer. The crucible containing the sulfate was coolled in a desiccator over sulfuric acid and when cool was set into a wide-mouthed weighing bottle closed with a ground-glass stopper. Ignitions were always made to constant weight and on two occasions the treatment with sulfuric acid was repeated.

Two or three complete operations were at first carried through to become familiar with the manipulation and then the following, using Preparation III, were made: The calculated values in Column 3 were obtained by multiplying the weights in Column 1 by 1.26407. In deriving this factor the atomic weights in the 1914 table were used. Weighings were not corrected to vacuum since the difference in the specific gravities of the two substances—$MgCl_2$ 2.18, and $MgSO_4$ 2.66—is so small that the error introduced by disregarding it is negligible in comparison with the errors as given in Column 4. The letters b and c in Column 1 indicate the boat method and crucible method of transforming the chloride into the sulfate.

MgCl₂ taken.	MgSO₄ obt.	MgSO₄ cal.	Error.
0.7530 b	0 9520	0.9518	+0 0002
0 1374 b	0 1733	0.1737	—0 0004
0 4027 c	0.5094	0.5090	+0 0004
0.5312 c	0.6714	0 6715	—0 0001
0 6957 b	0 8794	0.8794	0 0000
0.5457 c	0.6900	0.6898	+0 0002

In all, 3.0657 g. of $MgCl_2$ were transformed into $MgSO_4$, giving 3.8755 g. The calculated amount is 3 8753 g.

Discussion.

Of the six experiments carried through, four gave good results and two, the second and third, have rather large errors. We have no explanation to offer for these, since there was nothing observed in their carrying out to suggest that they were different from the others. It is to be noted that one is by the boat method and one by the crucible method and that one carries a minus and one a plus error. Indeed the plus and minus errors are so distributed in the whole series that they may fairly be ascribed to manipulation rather than to impure materials or to some inherent source of trouble in the nature of the reaction.

We regret greatly that time did not permit carrying through at least twice as many experiments but, as it is, we believe that the results add materially to the evidence in favor of the correctness of the sulfate method for standardizing a magnesium salt solution.

After all, though, if work of this type has any value it is not so likely to lie in the actual results obtained by the first attempt as in the general suggestion it offers for such studies of the more important analytical reactions. It is at any rate the intention in this laboratory to carry out other investigations of a similar kind.

Summary.

In this article there has been described:

1. The preparation of pure magnesium salt for use as a standard in analytical work.

2. An easily constructed piece of apparatus by which material can be heated in a combustion tube and transferred to a weighing bottle without exposure to the air.

3. A set of experiments in which anhydrous magnesium chloride was transformed into magnesium sulfate.

COLUMBUS, O.

BEHAVIOR OF AMMONIUM PHOSPHOMOLYBDATE WITH AMMONIUM HYDROXIDE.

By Pulin Bihari Sircar.

In the Woy[1] method of estimation of phosphates, the phosphoric acid is first precipitated as ammonium phosphomolybdate, which is then dissolved in ammonia and reprecipitated by magnesia mixture. Evidently, in solution, free phosphate ions exist.

Gibbs[2] has made a thorough investigation of these reactions and he has shown that the ammonium phosphomolybdate dissolves in ammonia and on allowing the ammoniacal solution to stand, glistening needles or prisms, having the composition $2(NH_4)_3PO_4.5MoO_3.7H_2O$ separate out. The present investigation was undertaken for a fuller study of the solubility of ammonium phosphomolybdate in ammonium hydroxide. A pure sample of ammonium phosphomolybdate was prepared by precipitating a solution of sodium-hydrogen phosphate with ammonium molybdate. The precipitate was then washed free from mother liquor and dried. The dry yellow powder was placed in a beaker and an excess of strong solution of ammonia was added to it and stirred; a white crystalline salt was at once thrown down with evolution of heat.

This white substance was immediately dried by pressing between the folds of bibulous drying paper and analyzed. The substance was not put in a desiccator but dried in air.

Calc. for $(NH_4)_3Mo_7O_{24}.3NH_3$: Mo = 49.11; N = 17.88; H = 4.42; found: Mo = 49.8; N (by Kjeldahl) = 17.25; H (by combustion) = 4.15.

[1] Chem. Ztg., 21, 442.

[2] Am. Chem. J., 5, 361, 391, etc.

A dozen preparations were undertaken in which the strength of ammonia was varied, but invariably the same crystalline substance was obtained, as was determined by quantitative analysis.

That it was not a mixture of two or more substances was proved in the following way: A sample, freshly prepared, was taken at random, carefully washed with distilled water, dried and analyzed.

Found for washed portion: Mo = 49.22; NH_3 (by Kjeldahl) = 20.6; found for unwashed portion: Mo = 49.35, NH_3 (by Kjeldahl) = 20.7.

Thus we see that a definite compound, having the composition

$$(NH_4)_2Mo_2O_7 \cdot 3NH_3,$$

is obtained as precipitate by adding strong solution of ammonia to ammonium phosphomolybdate. It has been found, however, that the substance gradually loses ammonia and if we put the salt in a weighing tube it very gradually loses weight and the smell of ammonia is given off. At the same time the crystals crumble to a white powder. Moreover, that the ammonia in the compound is loosely combined is shown by its peculiar behavior in the determination of nitrogen. On heating the substance during analysis about three-fifths of the total nitrogen is immediately given off and the remaining two-fifths is collected after a long time on prolonged heating. That the salt of the composition $(NH_4)_2Mo_2O_7 \cdot 3NH_3$ gradually loses ammonia was shown by the following comparative tests:

0.1870 g. of the salt gave, by the Kjeldahl method, 0.0383 g. of ammonia, or 20.5%.

On the very next day 0.5249 g. of the same sample gave 0.1029 g. of NH_3, or 19.6% ammonia.

The final and stable product of decomposition was then carefully analyzed:

Calc. for $(NH_4)_2Mo_2O_7$: Mo = 56.48; N = 8.23; H = 2.48; found: Mo = 56.35, N (Dumas method), 7.8; H (by combustion), 2.81.

Hence the substance $(NH_4)_2Mo_2O_7 \cdot 3NH_3$ obtained as precipitate decomposes into the dimolybdate $(NH_4)_2Mo_2O_7$. But, sometimes a little phosphoric acid, varying from 0.1 to 0.2%, has been found, which is probably adsorbed with the crystals.

If the ammonia used is very dilute we do not get an immediate precipitation on its addition to ammonium phosphomolybdate, but if the solution is allowed to evaporate, generally at first crystals of ammonium molybdate, having the composition $(NH_4)_2Mo_2O_7 \cdot 3NH_3$, separate out. Very seldom we get the salt described by Gibbs.

But if we add a large excess of strongest solution of ammonia available, at first the same crystalline substance is obtained, which on further addition of ammonia dissolves, and after a short time a gelatinous, flocculent

precipitate appears. After vigorously stirring and allowing to settle, a precipitate thus obtained was then drained from the mother liquor by strong suction and dried by means of blotting paper. It was extremely hygroscopic. The precipitate was found to be absolutely free from molybdate. On analysis it gave the following results:

Calc. for $(NH_4)_2HPO_4$: $PO_4 = 71.99$; $N = 21.3$; $H = 6.8$; found: $PO_4 = 71.86$, N (Dumas) $= 21.9$; $H = 6.5\%$.

Evidently on adding a large excess of strong solution of ammonia the salt of the composition $(NH_4)_2HPO_4$ is obtained. Now the dimolybdate $(NH_4)_2Mo_2O_7$ is rather sparingly soluble and the substance $(NH_4)_2Mo_2O_7.3NH_3$ is much more soluble, but on adding excess of ammonia, evidently a compound containing ammonia much in excess to the compound described above is formed which is very easily soluble and hence remains in solution and only ammonium hydrogen phosphate is precipitated. These relations will be clear from Table I.

Specific gravity of ammonia used.	Weight of ammonium phosphomolyb-date taken Grams	Volume of the solution of ammonia used. Cc	Observation
0.90	9.5	40	Extremely hygroscopic crystals of $(NH_4)_2HPO_4$ were obtained as precipitate.
0.91	9.45	25	Prismatic crystals of $(NH_4)_2Mo_2O_7.3NH_3$ were obtained as precipitate
0.92	9.5	11	No precipitate: but on allowing the ammoniacal solution to evaporate, first, all the molybdenum appears as $(NH_4)_2Mo_2O_7.3NH_3$ and then phosphoric acid as $(NH_4)_2HPO_4$.

TABLE I.

Incidentally, crystals of ordinary ammonium molybdate were analyzed and it was found to correspond to the formula $(NH_4)_6Mo_7O_{24}.4H_2O$:

Calc. for $(NH_4)_6Mo_7O_{24}.4H_2O$. $Mo = 54.37$, $N = 6.8$; found: $Mo = 54.37$, $N = 7.38$.

Summary.

The addition of ammonium hydroxide of medium strength to ammonium phosphomolybdate usually produces a crystalline deposit having the composition $(NH_4)_2Mo_2O_7.3NH_3$, on the addition of strongest ammonium hydroxide available, hygroscopic crystals of the composition $(NH_4)_2HPO_4$ are obtained.

In conclusion, I offer my best thanks to Professors Ray and Bhaduri.

CHEMICAL LABORATORY, PRESIDENCY COLLEGE,
CALCUTTA.

THE USE OF HYDROFLUORIC ACID IN THE SEPARATION OF COPPER AND LEAD FROM TIN AND ANTIMONY BY MEANS OF THE ELECTRIC CURRENT.

By LeRoy W. McCay.

A few years ago I published in This Journal[1] a paper on a method for separating antimony from tin. The method is based on the fact that when antimonious oxide and stannic oxide are present in a hydrochloric or sulfuric acid solution containing some hydrofluoric acid, the introduction of a stream of hydrogen sulfide into the solution occasions a precipitation of antimonious sulfide only. If the antimony be in the higher state of oxidation and sufficient hydrofluoric acid be present it undergoes at first no change when its solution is treated with hydrogen sulfide. On continued action of the gas, the solution becomes slightly turbid from the separation of a small amount of sulfide of antimony, but this turbidity disappears at once when the solution is warmed. Copper and lead and a number of other heavy metals in hydrofluoric acid solution behave like antimonious antimony; they are thrown down completely by hydrogen sulfide.

The analogy between the behavior of solutions of the metals when treated with hydrogen sulfide and when subjected to the action of the electric current led me sometime ago to the belief that from a hydrofluoric acid solution containing both antimony and tin in the higher states of oxidation, the electric current would precipitate neither metal. Such, indeed, turns out to be the case. If copper, or lead, or both, be present along with the antimonic antimony and stannic tin, and the solution be a nitrohydrofluoric acid one, the copper is deposited at the cathode, the lead as the peroxide at the anode.

There can be no doubt but that other heavy metals can be separated from tin and antimony in a similar way.

Those who have had much to do with the chemistry of tin and antimony are familiar with the ease with which their compounds undergo hydrolysis. Particularly marked is this phenomenon in the case of salts of antimony. The presence of hydrofluoric acid, however, even in comparatively small amounts, inhibits entirely all tendency on the part of these two metals to form insoluble basic compounds. We can dilute a tin or antimony solution containing a little hydrofluoric acid indefinitely without the resulting liquids becoming turbid.

Nitric acid converts tin into insoluble metastannic acid, antimony into a mixture of antimonious and antimonic oxides which are almost insoluble in the concentrated as well as in the dilute acid. If, however, to the nitric acid a little hydrofluoric acid be added we obtain the best of all solvents for antimony and tin and their alloys. Dilute nitric acid

[1] 31, 373 (1909).

(1 : 4) containing a small amount of hydrofluoric acid will, when gently warmed, dissolve in less than 5 minutes over one gram of a tin-antimony alloy, provided the material be in a finely divided condition.

It matters not how rich the alloys are in tin or lead, the resulting solutions are clear and limpid. In all my work I use as a solvent 25–50 cc. of dilute nitric acid (1 : 4) to which 5 cc. of 48% hydrofluoric acid[1] have been added. Of course, the solutions are made in platinum. In the circumstances, all the tin, but only a part of the antimony, is converted into the higher state of oxidation. To complete the oxidation of the antimony, a saturated solution of potassium bichromate has proved best. I add it drop by drop with constant stirring until the pure green color of the warm solution takes on a slight yellowish green tint. The stirring is done with a platinum spatula tied to the end of a short stick. The chromic salt and small excess of chromic acid have no influence on the separation of the copper and lead from the tin and antimony, or on their subsequent determination. It is an interesting fact that, in the separation of copper from tin, a little platinum is dissolved at the anode and partially reprecipitated along with the copper at the cathode The amount dissolved is variable, but seems to increase with the amount of tin present. It appears in the form of a black powder, or very thin film, when the copper deposit is dissolved in nitric acid. The film can be readily removed by gently rubbing the surface of the dish with a bit of rubber on the end of a glass rod. The amount, so far as the eye is concerned, appears to be considerable, and yet when the powder is filtered off, ignited and weighed, it rarely amounts to more than half a milligram. I have found that by first coating the anode with a film of lead peroxide the copper comes down free from platinum. Since, however, any platinum in the copper can be determined rapidly and with great accuracy, I do not think we gain anything by using an anode coated with lead peroxide. The current from one or two storage cells was employed in my work.

Experimental.

Separation of Copper from Tin.—The copper solution used contained 20.001 g. purest blue vitriol in a liter of water.

Calculated. 25 cc. = 0.1274 Cu; found. 25 cc. = 0.1275 Cu.

The tin used was a well-known German firm's best, and in order that the solvent might attack it most readily I had the machinist convert it into thin turnings. The weighed sample of tin was placed in an ordinary Classen dish, the requisite amount of solvent added, the dish covered with a piece of platinum foil, and the liquid very gently heated. When solution was complete a known volume of the blue vitriol solution was run in,

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[1] Satisfactory results have been recently obtained by using smaller amounts of hydrofluoric acid.

the liquid diluted to 110 cc. and electrolyzed over night with a current strength of 0.25 A. The liquid over the deposit was siphoned off with a short piece of black rubber tubing upon which the hydrofluoric acid has no action. The washing was done in the usual way, water being poured into the dish and siphoned off until the needle of the ammeter dropped to zero, the main liquid and washings being trapped in a large ceresin beaker.

	Copper taken Gram	Tin taken Gram	Copper found (Cor for Pt) Gram
(1)	0 1020	0 2043	0 1015
(2)	0 1275	0 3950	0 1274
(3) .	0 1275	0 5014	0 1274
(4)	0 1275	0 5016	0 1276[1]

Separation of Copper from Antimony. The separation was carried out in a manner similar to that employed in separating copper from tin. Before introducing the current, however, all antimonious oxide was oxidized to antimonic oxide with a concentrated solution of potassium bichromate. In (3) I detected a trace of platinum in the copper. The current ran over night Current strength, 0.25 A.

	Copper taken Gram	Antimony taken Gram	Copper found Gram
(1)	0 1020	0 1993	0 1018
(2)	0 1275	0 2102	0 1273
(3)	0 1275	0 5008	0 1274

In order to see how accurate the results for copper would be when both tin and antimony were present, I dissolved in the platinum dish in 50 cc. of the nitrohydrofluoric acid various amounts of a tin-antimony alloy containing from 0.13 to 0.14% copper, oxidized the Sb^{III} to Sb^{V} with potassium bichromate, added 25 cc. of the standard blue vitriol solution and brought the volume to 110 cc. From the weight of the copper found in each case, the amount of the metal present in the quantity of alloy taken was deducted. The alloy was analyzed several years ago with the following results

Tin	60 42
Antimony	39 33
Lead	0 26
Copper	0 13
Sum	

Since the lead separated as the peroxide on the spiral anode I also determined it in each case. The current ran over night. Current strength, 0.25 A.

[1] Anode coated with PbO_2

	Copper taken. Gram.	Alloy taken Grams.	Copper found (Cor. for Pt). Gram.	Lead found in alloy. Per cent.
(1).....	0 1275	0.5001	0 1274	0 26
(2) . ..	0.1275	1.0005	0.1275	0 27
(3). .	0 1275	1 0010	0 1276	0 26
(4). . .	0 1275	1 0100	0 1277	0 25

Separation of Lead from Tin and Antimony.—The solutions contained 20 cc. conc. nitric acid and 5 cc. 48% hydrofluoric acid. The large amount of nitric acid is necessary in order to inhibit the separation of metallic lead at the cathode. The antimony present in the lower state of oxidation was converted into the higher state by means of chromic acid and the volume of the solution was always brought to 110 cc. The lead peroxide was deposited in a Classen dish roughened by means of a sand blast. Since this dish is made the anode, and a large surface is consequently exposed to the action of oxygen, which in the presence of hydrofluoric acid has a slight action on platinum, it may lose in weight during the electrolysis, and should, therefore, be reweighed after dissolving out the peroxide. Hot, dilute nitric acid, containing considerable oxalic acid dissolved in it, is well adapted for removing the peroxide from the dish. Dilute nitric acid to which a little ordinary hydrogen peroxide, free from hydrochloric acid, has been added serves the purpose equally well.

My first results for lead were much too high, in spite of the fact that I could detect no tin or antimony in the peroxide deposits. It is a well recognized fact that when lead is determined as peroxide, with the electric current, the results are apt to be high, and this is thought by most chemists to be due to the presence of water which is not completely expelled at 190–200°. My results, however, were almost 2 mg. in excess of what they should be. Thus far I have been unable to account for these high figures.

The lead solution used as a standard contained 6.0004 g. pure lead nitrate in a liter.

	Found	
Calculated Gram	By electrolysis Gram	By evaporation and ignition Gram.
25 cc. = 0 0938	25 cc = 0 0939	25 cc = 0 0937 Pb

Separation of Lead from Tin.—The current ran over night. Current strength, 0.3 A.

	Lead taken Gram	Tin taken Gram	Lead found Gram
(1)[•]	0 0938	0 5014	0 0956
(2)	0 0938	0 5084	0 0955
(3)	0.0938	0 5102	0 0957

Average, 0 0956 gram

0.0956 g. found — 0.0938 g taken = 0 0018 g. overweight

In separating the metal from antimony the same high results were obtained. A determination of lead in dilute nitrohydrofluoric acid solution,

when no tin was present, gave me the figure 0.0957. Since a satisfactory result was always obtained when *no* hydrofluoric acid was present, it seems reasonable to assume that the overweights of the deposits are due to the presence, in them, of fluorine in some form. Thus far, however, I have been unable to detect any with certainty. The error can be eliminated, and results obtained equal almost in accuracy to those arrived at when lead is determined as peroxide in nitric acid alone, by proceeding as follows: After siphoning off the supernatant liquid and washing a deposit until the needle of the ammeter stands at zero, 20 cc. conc. nitric acid are again poured into the dish, the dish is filled with water until the peroxide is just covered, and the current reversed. In a few minutes the solution is complete, the current is then again reversed and the lead reprecipitated as peroxide. Using a current strength of 0.5 A., the time necessary for complete reprecipitation is from 4–5 hours.

Here are some results obtained by following the modification just described:

	Lead taken Gram	Tin taken Gram	Lead found Gram
(1)	0 0938	0 2015	0 0935
(2)	0 0938	0 2625	0 0938
(3)	0 0938	0 3025	0 0939
(4)	0 0938	0 4987	0 0937
(5)	0 0938	0 5036	0 0939
(6)	0 1876	0 5168	0 1881

The next determinations show that all the tin taken is present in the liquid siphoned off from the first peroxide deposit, and that from the standpoint of ordinary analysis no appreciable amount can be included in the PbO_2.

	Lead taken Gram	Tin taken Gram	Lead found Gram	Tin found. Gram
(1)	0 1876	0 1614	0 1875	0 1623
(2)	0 1876	0 2994	0 1881	0 2995
(3)....	0 1876	0 5169	0 1875	0 5170

I determined the tin by adding to the solution containing it 10 cc. conc. sulfuric acid, evaporating as far as possible in platinum on the water bath, heating the residue to strong fuming to expel the hydrofluoric acid, cooling, and pouring the liquid into a liter of water   The tin was weighed as stannic oxide.

Separation of Lead from Antimony.—The details to be observed in separating lead from antimony will be evident from what has already been said. It should be remembered, however, that before introducing the current all antimony present in the lower state of oxidation must be brought to the higher state with a solution of potassium bichromate. The deposits first obtained were redissolved by reversing the current, and the results for the lead calculated from the weights of the reprecipitated peroxide

(see the Separation of Lead from Tin). Current strength for first precipitation (over night), 0.25 A, for second (4–5 hrs.), 0.5 A.

	Lead taken. Gram	Antimony taken Gram	Lead found. Gram.	Antimony found. Gram
(1)	0 0750	0 1201	0 0753	0 1200
(2)	0 0938	0 1402	0 0935	0 1411
(3)	0 0938	0 2100	0 0936	0 2099
(4) .	0 1876	0 1209	0 1871	0 1208

In each case the liquids and washings from the first precipitations of the lead as peroxide were treated with 10 cc. of conc. sulfuric acid and evaporated on the water bath in platinum as far as possible. The residues were heated to strong fuming, the dish was covered, a piece of pure sulfur dropped in and the sulfuric acid boiled as gently as possible for 20 minutes The antimony, now in the lower state of oxidation, was then determined volumetrically with potassium permanganate according to Kessler's method.[1]

Excellent results have been obtained by dissolving the lead peroxide deposits first obtained in about 10 cc. dilute nitric acid to which 5 cc. ordinary hydrogen peroxide free from hydrochloric acid were added, transferring the solution to a quartz or porcelain dish, adding 5 cc. conc. sulfuric acid, evaporating as far as possible on the water bath, heating the residue to strong fuming, and determining the lead as the sulfate. The salt was collected and ignited in a Neubauer crucible.

	Lead nitrate taken Gram	Lead cal Gram	Alloy taken [2] Gram	Lead found.[3] Gram
(1)	0 2103	0 1315	0 3900	0 1316
(2)	0 3002	0 1877	0 4993	0 1878
(3)	0 6007	0 3756	0 5005	0 3752

Some experiments having shown, at this stage of the work, that lead peroxide is attacked quite slowly by dilute nitrohydrofluoric acid, I broke the current in all the last three separations as soon as precipitation was complete, and *at once* poured off the liquid above the deposits. The results are perfectly satisfactory, and prove that it is not necessary that the deposits should be washed while the current is still passing. This is important, as we are not required to evaporate such large volumes of liquid, in case a determination of tin or antimony is desired.

The copper and lead in a white metal, very homogeneous in composition, have been determined with marked success according to this hydrofluoric acid method. About 0.5 g. of the finely divided material was employed in each case. The lead peroxide first deposited was transformed into the sulfate, according to the directions above given, and weighed in

[1] *Pogg Ann*, 118, 17 (1863). See also Fresenius' Quant. Analyse (1875), B. I., p 360

[2] The composition of this alloy is given on p 2377.

[3] Corrected for the 0.26% present in the alloy.

this form. From the liquid poured off from the lead peroxide the copper was precipitated, after the excess of acid had been neutralized with ammonia.

		Electrolytically			
Copper	2 70	2 70	2 74	2 76	2 75
Lead	12 66	12 60	12 50	12 67	12 66
Antimony	11 65	11 62	Determined in the liquid from which the Cu had		
Tin	73 20	73 25	been precipitated The Sb was determined		
			volumetrically, the Sn gravimetrically [1]		
	100 21	100 17			

From a dilute nitrohydrofluoric acid solution, copper can be separated from tungsten, and mercury and silver ,from tin and antimony. My assistant, Mr. N. H. Furman, finds that the results obtained in separating mercury from tin and antimony are fully as exact as those arrived at in separating copper from these metals. Attempts are being made to separate and determine other metals by means of the current when they are present in solutions containing hydrofluoric acid.

PRINCETON, N J

THE CONSTITUTION OF ALUMINATES. II.

BY EDWARD G. MAHIN

In a recent paper by Blum,[2] entitled "Constitution of Aluminates," criticism was made of an earlier paper bearing the same title[3] by Mahin, Ingraham and Stewart   Inasmuch as the author seems to have entirely misinterpreted a part of the experimental work described in the first paper, and the deductions therefrom, it seems necessary to correct these impressions

Mahin, Ingraham and Stewart concluded that the hypothesis of aluminates having definite formulas had not been substantiated by any of the earlier work and that sufficient attention had not been given to the colloidal properties of aluminium hydroxide, as bearing upon its solubility in solutions of bases   Their supposition was that by adsorption of hydroxyl ions the aluminium hydroxide may be, to a considerable extent, maintained in a dispersed condition, molecular aggregates acquiring thereby a negative charge which has caused these aggregates to be mistaken for definite anions, because of their behavior when a current of electricity is passed through the solution of "aluminate."

This possibility seemed to be favored by the results of experiments upon the heat of solution of aluminium hydroxide in bases, upon the pre-

[1] The metals were separated according to the method described in THIS JOURNAL, 31, 373 (1909)

[2] THIS JOURNAL, 35, 1499 (1913).

[3] Ibid , 35, 30 (1913)

cipitation of aluminium hydroxide by reactions of ammonium nitrate with sodium aluminate and upon the electrolysis of aluminate solutions.

The reaction between ammonium nitrate and sodium aluminate was found to precipitate a proportionately *greater* quantity of aluminium hydroxide than would be indicated by the formula $NaAlO_2$, favored by most investigators. A substance of this formula could not produce more aluminium hydroxide than is indicated by the molecular proportion $Al_2O_3/NH_4\cdot NO_3 = \frac{1}{2}$. In the experiments, however, the ratios $1/1.885$ and $1/1.930$[1] were obtained. This would indicate a substance having *less* sodium than that having the formula $NaAlO_2$ (see equations of former paper). Blum criticizes these deductions by saying that the theoretical ratio could not be expected because of incomplete hydrolysis of the aluminate, complete hydrolysis being possible only in case of absolute nonionization of ammonium hydroxide. This is certainly true, but Blum apparently overlooks the fact that incomplete hydrolysis would result in incomplete precipitation of aluminium hydroxide, with a consequent experimental ratio of Al_2O_3/NH_4NO_3 *less* than $\frac{1}{2}$, whereas Mahin, Ingraham and Stewart found ratios in two cases *greater* than $\frac{1}{2}$. In his reply (see following paper) Blum suggests that these ratios may have been obtained as a result of spontaneous decomposition of the aluminate solutions, the duration of the experiment not having been stated. Less than 15 minutes was required for these experiments and other portions of the aluminate solutions, not treated with ammonium nitrate, remained clear. Spontaneous decomposition is, therefore, extremely improbable.

A similar error was made by Blum in his discussion of the results of the electrolysis of aluminate solutions. The formula $NaAlO_2$ indicates the least alkali metal of all formulas that have been proposed for the alkali aluminates. Mahin, Ingraham and Stewart argued that electrolysis of such a substance could not produce a greater quantity of aluminium hydroxide, relative to oxygen liberated at the anode, than that indicated by the proportion $Al_2O_3/O_2 = 2/1$, while resolution of aluminium hydroxide in the basic solution at the anode was an unavoidable error that worked always toward diminishing the experimental ratio. The authors did not argue (although Blum so states) that failure to obtain a definite ratio for Al_2O_3/O_2 indicated absence of aluminates of definite formulas. They merely pointed out that the ratios obtained in three experiments showed, as in the ammonium nitrate reactions, that if aluminates as salts existed in the solutions their formulas must be different from any that have been proposed.

In the electrolysis of alkaline solutions of aluminium the difficulties encountered in the attempt to prevent resolution of aluminium hydroxide

[1] In the original paper this ratio was given as $1/1.530$, as a result of a typographical error.

are practically insurmountable. Out of eighteen experiments reported in the original paper, three gave ratios of aluminium oxide precipitated to oxygen liberated at the anode, greater than $2/1$. These were $2/0.9968$, $2/0.8658$, and $2/0.9174$. Since that time, one of the authors (Mahin), working with Mr. O. M. Harrison, has obtained the ratios $2/0.8820$ and $2/0.9524$ in two experiments out of seven. If resolution could be entirely prevented the ratios would be still larger. If definite salts are present in the solutions they must be represented by such formulas as $Na_2Al_4O_7$, $NaAl_3O_5$, etc. The number of such formulas that might be invented is endless. (Blum suggests the possibility of spontaneous decomposition of the aluminate solutions in these experiments also. Such possibility was excluded by the fact that the experiments were watched very carefully, the electrolysis being stopped in each case whenever the least turbidity appeared in the main body of the solution.)

The evidence presented by Blum in his measurements of the amount of basic solution required to precipitate and redissolve aluminium hydroxide from aluminium chloride,[1] appears to be the most definite of any that has been presented. However, it may be pointed out that in his curve C,[2] if the third point of inflection is taken strictly as the curve indicates, it will fall at a point corresponding with $[H^+] =$ (nearly) $10^{-11.5}$ instead of $10^{-10.5}$. At this point the volume of basic solution is 28.5 cc. instead of 28 cc. In this case the ratio of base required to redissolve the precipitate, to that required to form it is $\dfrac{28.5 - 21.5}{21.5 - 4} = 0.4$, not 0.33. This would correspond with an aluminate containing more alkali metal than is indicated by the formula $KAlO_2$. In other words, this definite formula can be obtained from the curve only by a somewhat arbitrary selection of a point of inflection which is not indicated by the experiments.

PURDUE UNIVERSITY.

THE CONSTITUTION OF ALUMINATES.[3]

BY WILLIAM BLUM.
Received September 10, 1914

In my discussion[4] of the evidence of Mahin, Ingraham and Stewart,[5] regarding the reaction between sodium aluminate and ammonium nitrate, stress was laid upon the uncertainty due to incomplete hydrolysis of the aluminate, which would lead to incomplete precipitation of the aluminium hydroxide, such as evidently occurred in Expt. 2 of Table I, where the ratio

[1] Loc. cit.
[2] THIS JOURNAL, 35, 1500 (1913).
[3] Published by permission of the Director of the Bureau of Standards
[4] THIS JOURNAL, 35, 1503 (1913)
[5] Ibid., 35, 36 (1913).

2.68/1 was obtained. The slight excess of aluminium hydroxide precipitated in the other two experiments may have been due to spontaneous decomposition of the aluminate solutions, even though the period of the reaction was only fifteen minutes, a phenomenon I have often observed with aluminate solutions saturated with aluminium hydroxide. It is at least interesting to note that the effect of any such error, if present, would be proportionally greater in Expts. 1 and 3, than in 2, owing to the smaller amounts of aluminium hydroxide involved in the former experiments. Indeed, if the molecular ratio NH_4NO_3/Al_2O_3 be calculated for the sum of the amounts involved in the three experiments, the ratio 2.39 is obtained; i. e., the total error is in the direction expected, a deficient precipitation of aluminium hydroxide. In this connection, attention should be called to an error in calculating the result for Expt. 3 of Table I, where the molecular ratio NH_4NO_3/Al_2O_3 should be 1.93 (and not 1.53 as given).

Similarly, in the discussion of the electrolysis experiments, attention was called in my former paper to the probable spontaneous decomposition of the solutions during electrolysis; especially since "In every case the precipitated aluminium hydroxide possessed at first the appearance of a colloidal gel, changing to the crystalline modification as the experiment proceeded." Such an effect might have counteracted, or even counterbalanced, the admitted solvent action of the liberated alkali. The fact that in only three out of eighteen experiments described in his original paper and in only two out of seven mentioned in the second paper[1] Mahin obtained ratios indicating an excess precipitation of aluminium hydroxide, is certainly not conclusive evidence of the nonexistence of sodium aluminate with a formula, $NaAlO_2$, or some multiple.

The curve C in my paper, referred to by Mahin, represents the action of potassium hydroxide upon aluminium chloride, in which, as pointed out in the original article, great difficulty was experienced in obtaining a clear solution, owing to the above-mentioned spontaneous separation of crystalline aluminium hydroxide. Greater significance should therefore be given to curve B, representing the action of sodium hydroxide.

The above considerations, together with the failure of Hildebrand[2] to detect colloidal particles in aluminate solutions by means of the ultramicroscope, seem to justify the original conclusion that definite aluminates, having the formula $MAlO_2$ or some multiple of it, probably exist in aqueous solution.[3]

WASHINGTON, D C

[1] THIS JOURNAL, preceding paper.

[2] Ibid , 35, 864 (1913)

[3] My attention has been called to an article by Slade and Polack in Trans Faraday Soc , 10, 150 (August, 1914), discussing the original paper by Mahin, Ingraham and Stewart, which came too late for consideration by the authors of these papers. [EDITOR.]

NOTE.

Natural Indicators.—Since the publication of the article on "Some Natural Indicators" in the September number of THIS JOURNAL, Mr. G. A. Fraps has called my attention to an article entitled "The Wide Occurrence of Indicators in Nature," by himself, published in the *American Chemical Journal* for September, 1900, in which he has recorded some similar observations.   H. W. BRUBAKER.

THE STRUCTURE OF MALTOSE AND ITS OXIDATION PRODUCTS WITH ALKALINE PEROXIDE OF HYDROGEN.

BY W. LEE LEWIS AND SIEGEL A. BUCKBOROUGH

Nef[1] and his students have established the methods for oxidizing the sugars with various agents and for separating and identifying the resulting products.   Nef[2] has recently submitted a complete system of dissociation of the sugar molecule in explanation of these oxidations and in explanation of the reciprocal conversion of certain sugars under the influence of dilute alkalies.

One[3] of us investigated the products formed when maltose is oxidized with alkaline cupric sulfate. This work brought out that maltose is oxidized largely as an unhydrolyzed disaccharose, forming glucosido-acids, whose subsequent hydrolysis gives dextrose and simpler acids. There were thus obtained from 100 g. of anhydrous maltose, 34.72 g. of hydrolyzed dextrose, 29.78 g. of hexonic acids, 2.86 g. of glycollic, 0.25 g. of oxalic, 3.46 g. of formic acids, and 7.74 g. of carbon dioxide. Of unidentified material, believed to contain glycerinic and trioxybutyric acids, there remained 27.29 g., with 2.15 g. lost during the various manipulations. The ratio of the various products found was quite different from that observed by Nef[4] in a study of the oxidation products of the simple hexoses, dextrose, levulose, and mannose, especially in respect to the larger amount of mannonic lactone (21.00 g.) formed from the disaccharose. This investigation of maltose, however, failed to throw any light on the constitution of that sugar, largely because the amount of oxygen taken up by each molecule was insufficient.

The present study was therefore undertaken in the hope that the more complete destruction of the maltose molecule, under the influence of alkaline hydrogen peroxide, might permit a better quantitative separation of the products, thus reflecting the point of the glucosido union between

[1] *Ann.*, **357**, 214–312; **376**, 1–119; **403**, 204–383.

[2] *Ibid.*, **403**, 204–242.

[3] Lewis, *Am. Chem. J.*, **42**, 301–319.

[4] *Ann.*, **357**, 259.

the two constituent dextrose groups in malt sugar. The results confirmed the previous findings that maltose oxidizes largely without hydrolysis and that saccharinic acid formation does not take place under the conditions. A larger amount of oxygen is taken up with alkaline peroxide as evidenced in the larger yield of acids containing few carbon atoms. One hundred grams of anhydrous maltose gave, by this method, 22.97 g. of hydrolyzed dextrose (corr. 24.97 g.) 0.16 g. of mannonic lactone, 16.04 g. of glycollic, 0.11 g. of oxalic, 55.37 g. of formic acid and 4.44 g. of carbon dioxide. Of unidentified material there remained 1.18 g., believed to contain erythronic and *l*-threonic acids. One gram of material was used up in titrations and otherwise lost in manipulation. Especially noteworthy are the larger amounts of formic and glycollic acid found in comparison with the previous work using alkaline copper sulfate. Herein it is believed are to be found the proofs indicated by Nef[1] which establish the structure of maltose as originally assumed by Fischer,[2] as a γ-*d*-glucosido-*d*-glucose hydrate,
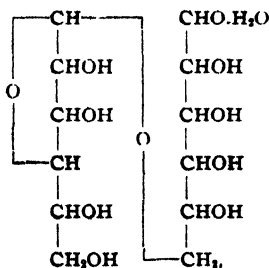
in which the primary alcohol hydroxyl functions in the glucosido union.

Fischer[3] established the structure of maltose[3] as a disaccharose composed of two molecules of *d*-glucose and containing a γ-lactone ring similar to his synthetic alkyl glucosides. According to Armstrong[4] maltose is an α-glucoside, as established by selective enzyme action. The resulting formula $C_6H_{10}O_5.CH_2OH(CHOH)_4.CHO.H_2O$ does not, however, determine which of the carbon atoms 1, 2, 3, 4, and 5, holds the hydroxyl group taking part in the glucosido union. Carbon atoms 1, 2 and 3 may be at once eliminated as possibilities from the following consideration: *d*-Maltose with $1^1/_2$ molecules of calcium hydroxide at ordinary temperature gives a very large quantity of glucosido α and β-*d*-isosaccharinic acids,[5]

[1] *Ann*, **403**, 299–303
[2] *Ber*, **27**, 2988
[3] *Ibid.*, **35**, 3141; **28**, 1145; Nef, *Ann.*, **403**, 299
[4] *Trans Chem. Soc*, **85**, 1305
[5] Kiliani, *Ber*, **18**, 631, 2514. **38**, 2668; Nef, *Ann.*, **357**, 306, **376**, 54–56.

COOH   COOH
| |
HO—C—CH₂OH   CH₂OH—C—OH
| |
CH₂   CH.
| |
CHOH   CHOH
| |
CH₂OH   and   CH₂OH
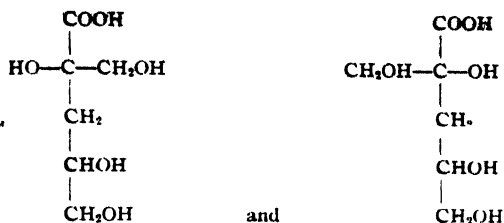
This product can only come about through enolization of malt sugar with subsequent addition and splitting off of water forming intermediately

$$\gamma\text{-}d\text{-glucosido-}d\text{-fructose,} \quad C_6H_{10}O_5.CH_2OH(CHOH)_3{-}\overset{\overset{O}{\|}}{C}{-}{-}CH_2OH,$$ after the analogy of the interconversion of simple hexoses under the influence of alkalies.[1] This product similarly goes over into γ-d-glucosido ortho-

$$\text{hexoson,} \quad C_6H_{10}O_5.CH_2OHCHOHCH_2{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{!}}{C}{-}{-}CH_2OH,$$ which, by the benzilic acid rearrangement, can give the final product γ-d-glucosido α and β-isosaccharinic acids. Hydrolysis of the latter yields d-glucose and α- and β-isosaccharin. It may be seen that these transformations involve the three hydroxyl groups attached to carbon atoms 1, 2 and 3, which therefore must be present as such in the original maltose molecule. The participation of any one of these in the glucosido union is therefore precluded.

The selection of the correct hydroxyl group, as between the two remaining, is fixed upon that attached to carbon atom 6 by the following considerations:

Nef[2] and Glattfeld[3] have shown that, when glucose is treated with alkali of a certain concentration, there results six sugars; i. e., d-glucose, d-mannose, d-fructose, d-pseudofructose and α- and β-d-glutose. The intermediate 1,2-hexose dienols of this transformation undergo dissociation into hydroxy methylene and methyleneols of the pentoses. There result, finally, through further dissociation, various sugars containing one, two, three, four and five carbon atoms $(CH_2O)_x$, the oxidation of which, accompanied in some instances by the benzilic acid rearrangement, produces the ultimate products found in sugar oxidation.

It is altogether probable that maltose under the influence of alkalies enters into a similar equilibrium[4] of the six glucosido hexoses of the glucose series. The intermediate glucosido hexosedienols undergoing

[1] Ber., 28, 3078; Rec. trav. chem. Pays-Bas., 19, 1 (1900).
[2] Ann., 403, 362.
[3] Am. Chem. J., 50, 137.
[4] Nef, Ann., 403, 300, 381–382.

dissociation, oxidation, etc., would produce the glucosido acids whose hydrolysis would give the final products found in this study.

The step-by-step splitting off of oxymethylene with the formation of formic and carbonic acids, as the main course of the reaction, could not go beyond the carbon atom whose hydroxyl enters into the glucosido union, otherwise glucosido acids would not be the principal product of the oxidation. In the following equation it may be seen that if Formula I were correct for maltose the principal product of the oxidation would be glucosido glycerinic:

I.

```
   ┌─CH────┐  CHO.H₂O         ┌─CH────┐
   │ CHOH  │  CHOH            │ CHOH  │
O  │ CHOH  O  CHOH         O  │ CHOH  O
   │       │  CHOH            │
   └─CH────┘  CHOH    ──→     └─CH────┐
   │ CHOH  ┌─CH                │ CHOH  │  COOH
   │ CH₂OH │  CH₂OH            │ CH₂OH └─CH
                                        │ CH₂OH
```
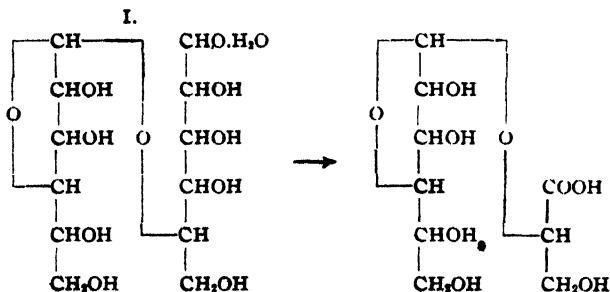
If Formula II were correct, the principal product would be glucosido glycollic acid.

II.

```
   ┌─CH────┐  CHO.H₂O         ┌─CH────┐
   │ CHOH  │  CHOH            │ CHOH  │
O  │ CHOH  │  CHOH         O  │ CHOH  │
   │       O  CHOH            │       O
   └─CH────┤  CHOH    ──→     └─CH────┐
   │ CHOH  │  CHOH            │ CHOH  │  COOH
   │ CH₂OH └──CH₂             │ CH₂OH └──CH₂
```
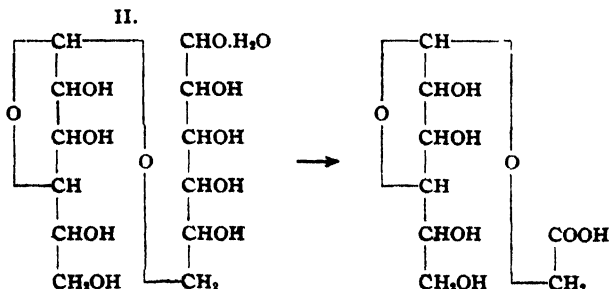
One hundred grams of maltose with alkaline peroxide gave finally 16.04 g. of pure crystalline glycollic acid while glycerinic acid was not found present.

The ratio and nature of the oxidation products of d-glucose with alkaline hydrogen peroxide are quite different from those of maltose, especially in respect to the small amount of glycollic acid[1] (4.3 from 100 g.) and the presence of d-arabonic lactone[2] in the former. These differences must be due to the effect of the above glucosido bond.

Regarding the source of the other products found, the large quantities

[1] Spoehr, *Am. Chem. J.*, **43**, 238.
[2] Glattfeld, *Ibid.*, **50**, 135–157.

of carbonic and formic acids undoubtedly result from the oxidation of dissociated hydroxymethylene, $>CHOH$. Oxalic acid could result from a more complete oxidation of diose methyleneol, $HOCH_2COH<$.[1] Erythronic and *l*-threonic acid were indicated in the results but not established because of the small amounts. Their formation is most probable from the dissociation of glucosido 2,3-*d*-glucose dienol,
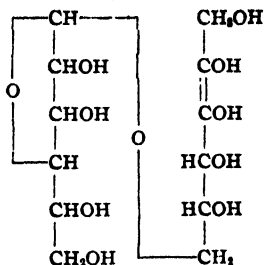
into the methylenols of diose, $HOCH_2C(OH)<$, and of glucosido-*d*-erythrose. The osone of the latter, formed by oxidation, could undergo the benzilic acid rearrangement (asymmetric in part or entire) to give C_4 acids.

Mannonic lactone, on the other hand, has been proved to arise from the hydrolysis of glucosido mannonic acid through the action of dilute alkalies on maltosone.[2] That the benzilic acid rearrangement often takes place asymmetrically has been pointed out by Nef[3] in explanation of the preponderating gluconic acid in oxidation of the simple hexoses and of mannonic acid when maltose is acted upon by Fehling's solution.[4] In the oxidation of maltose with alkaline peroxide there is formed intermediately therefore some malt·sone.

Experimental Part.

A solution of 3.22 g. of maltose in 80 cc. of 3% hydrogen peroxide (6.5 molecules) was prepared and added with vigorous shaking through a period of ten minutes to a solution of 5.62 g. of 85.7% potassium hydroxide (equivalent to 4.82 g. of potassium hydroxide net, being 7.7 molecules) in 100 cc. of water. The total volume was then increased to 200 cc., making the concentration of the alkali approximately half normal. Under similar conditions 3.22 g. of maltose were dissolved in 160 cc. hydrogen peroxide and the mixture poured with vigorous shaking through a period of ten minutes into a solution of 5.62 g. of potassium hydroxide in 40 cc. water.

[1] Cf. Anderson, *Am. Chem. J.*, 42, 406.

[2] Lewis, *Ibid.*, 42, 315–319.

[3] *Ann.*, 357, 231–2, 284.

[4] In unpublished notes one of us (Lewis) has obtained mannonic lactone in quantity from the oxidation of lactose with Fehling's solution.

Three solutions of each concentration were prepared and kept at room temperature, being protected from the carbon dioxide of the air by means of soda lime tubes.

In none of the above mixtures was any change in temperature or appearance of the solution noted. The final solutions were in all cases colorless.

By testing with Fehling's solution the oxidation was found in the first three trials (80 cc. hydrogen peroxide) to be complete after seven to ten days and in the last three (160 cc. hydrogen peroxide) after fourteen to seventeen days, as evidenced by the absence of reduction. While the solutions were standing, as well as at the conclusion of the oxidation, the continued presence of an excess of hydrogen peroxide was proved by frequent tests with starch potassium iodide paper. The excess of hydrogen peroxide was finally removed by the addition of a little platinum black and vigorous stirring.

(1) *Quantitative Determination of the Amounts of Carbon Dioxide Formed in the Oxidation.*—To determine the amount of carbon dioxide in each case, an apparatus was set up in which a wash bottle of concentrated potassium hydroxide was connected with a large U-tube filled with soda lime, and this in turn with the flask containing a sugar solution. To the other side of the flask was attached a reflux condenser in series with six towers containing a saturated solution of barium hydroxide. The calculated amount of hydrochloric acid was then added to the alkaline reaction mixture by means of a dropping funnel, and air free from carbon dioxide was slowly and continuously drawn through the apparatus. The flask was finally heated in an oil bath at 110° to 120° for one hour. The barium carbonate precipitate was then thoroughly washed, dried at 100° and weighed.

Blank experiments were also made to determine the amount of carbon dioxide in 5.62 g. of potassium hydroxide. Three determinations gave respectively, 0.2430 g., 0.2439 g. and 0.2435 g. of barium carbonate.

The three solutions of maltose with 80 cc. of hydrogen peroxide, after the correction was made for the potassium hydroxide, gave respectively, 0.8584 g., 0.8556 g. and 0.8540 g. of barium carbonate. Two of the solutions prepared with 160 cc. hydrogen peroxide, after the correction, gave 0.9851 g. and 0.9629 g. of barium carbonate.

TABLE I —SUMMARY OF RESULTS FOR CARBON DIOXIDE

Amount of maltose Grams	Amount of hydrogen peroxide Cc	Time for oxidation. Days	Grams of carbon dioxide.	Per cent of theoretical yield.	Per cent. of total
3.22	80	7–10	0.137	2.91	4 52
3 22	80	7–10	0.134	2 84	4.41
3 22	80	7–10	0 136	2.85	4.47
3.22	160	14–17	0 220	4.67	7.21
3.22	160	14–17	0 215	4 56	7.05

(2) *Quantitative Determination of the Amounts of Volatile Acids.*—As before, three lots of 3.22 g. of maltose with 80 cc. hydrogen peroxide were set aside under like conditions, also three lots with 160 cc. hydrogen peroxide. The time periods for complete oxidation were the same as in the first series. After adding the platinum black to the solutions and heating the flasks to remove the excess of hydrogen peroxide, theoretical amounts of hydrogen chloride were added. Each solution was then separately distilled from a flask provided with a Kjeldahl bulb to prevent the volatilization of possible glycollic acid. A pressure of 10–25 mm. was maintained and the flask finally heated for some time in a boiling water bath. The residues were several times dissolved in 100 cc. of water and the distillation repeated. The distillate, which proved to be free from hydrogen chloride, was then made up to a definite volume and the formic acid determined by titrating an aliquot part with 0.1 N sodium hydroxide. The Jones[1] method was also used, in which the formic acid was oxidized to carbon dioxide with 0.1 N permanganate. The two methods agreed perfectly, thus proving formic the only volatile acid present.

TABLE II —SUMMARY OF RESULTS FOR FORMIC ACID.

Amount of maltose Grams	Amount of hydrogen peroxide Cc	Time for oxidation Days	Formic acid by permanganate Grams	Formic acid by sodium hydroxide Grams	Per cent of theoretical yield	Per cent of total weight
3 22	80	7–10	1 377		27 84	44 90
3 22	80	7–10	1 336	1 334	27 14	43 80
3 22	160	14–18	2 070	2 065	42 00	67 85
3 22	160	14–18	2 007	2 012	40 60	65 55
3 22	160	14–18	2 047		41 40	66 85

(3) *The Nonvolatile Acids.*—In the determination of the nonvolatile acids left behind with the salt residue after the distillation of formic acid, it was decided to use larger quantities of the materials in the same proportion as in the preliminary experiments, in which 80 cc. hydrogen peroxide were used. Eight 25.76 g. lots of maltose (equivalent to 195.77 g. of anhydrous sugar) were thus set aside. In each case the strength of the hydrogen peroxide was again determined just before using and correction made so as to keep the concentration uniform. No change in the temperature or color of the solution was ever noticed on addition of the hydrogen peroxide solution to the sugar. There were only slight differences in the time required for complete oxidation, the average being eleven days. After no reduction was shown with Fehling's solution, the contents of each flask were heated for a half hour and shaken repeatedly with platinum black to remove the excess of hydrogen peroxide. Then 6% in excess of the theoretical amount of hydrochloric acid was added, and the solution distilled at a temperature of 45° to 50° under a pressure

[1] *Am. Chem. J.,* **17,** 539.

of 15-25 mm. The residue in the flask was dried at 80° for half an hour, redissolved in 150 cc. water and again distilled. This process of re-distillation was continued until the nonvolatile acids were entirely free from hydrogen chloride.

The amount of formic acid in the filtrate from each lot was determined by the Jones method, the yields being as follows: 13.20 g., 13.48 g., 13.70 g., 14.19 g., 13.50 g., 13.45 g., 13.28 g., and 13.67 g., respectively. These results are nearly 25% higher than those obtained with small quantities of sugar.

The salty residues of acid gum from each lot of sugar were taken up in 95% alcohol, thus separating most of the potassium chloride. The 95% alcohol residues from each lot were then combined and refluxed with absolute alcohol, thus eliminating more of the salt. After filtering and concentrating somewhat, the filtrate was left at a low temperature for twenty-four hours. A little more of the salt separated out, together with a small amount of material which reduced Fehling's solution and which apparently was hydrolyzed sugar.

The final product, dried at 75° and 20 mm., weighed 105 g., which is 53.6% of the weight of the sugar used.

The gums, which were slightly darkened, were dissolved in five parts of 5% sulfuric acid and heated on the boiling water bath for ten hours under the reflux. Then the theoretical amount of barium hydroxide, necessary to remove the acid, was dissolved in 300 cc. of hot water and slowly added. After heating on the boiling water bath for another half hour the mixture was filtered. On concentrating the solution to two liters, the amount of split off sugar was determined by the Munson and Walker[1] method and also by the Fehling solution method. The results by the former in two determinations were 0.3808 g. and 0.3812 g. of cuprous oxide. This weight of cuprous oxide from 8 cc. of the solution corresponds to 178.4 mg. of dextrose, equivalent to 44.6 g. of this sugar in the 2000 cc. By the latter method 20 cc. of the sugar solution were diluted to 100 cc. and 11.20 cc. of this were required for 10 cc. of Fehling's solution, corresponding to a total of 45.0 g. of dextrose.

In order to determine to what extent dextrose was destroyed during the ten hours hydrolysis with five parts of 5% sulfuric acid, an independent experiment was conducted in which 100 g. of c. p. dextrose hydrate (90.90 anhydrous) was refluxed on the boiling water bath ten hours with 500 cc. of 5% sulfuric acid. The solution darkened and showed a final content of 80.12 g. of anhydrous dextrose (91.43 g. hydrated) or a loss of 8,56%.

The solution was now adjusted so that a few drops gave the slightest precipitate with a 2% solution of sulfuric acid, filtered and concentrated

[1] This Journal, 28, 663; 29, 541.

to about 1500 cc. To remove the dextrose, the solution was heated in a boiling water bath with 60 g. of calcium carbonate for ten hours and filtered. The filtrate was of a golden red color and syrupy odor. Thirty-eight grams of calcium carbonate were filtered off and digested with 5% acetic acid. An insoluble residue was left which was dissolved in hydrochloric acid and reprecipitated with ammonia several times until perfectly white. This gave 0.3047 g. of calcium oxalate. When dried to a constant weight at 100° and analyzed the following result was obtained: 0.3047 g. of the salts gave on ignition 0.1168 g. CaO.

Calculated for $CaC_2O_4 H_2O \cdot CaO$, 33 89; found, 38 33

The aqueous solution of lime salts and dextrose was then concentrated in two hemispherical evaporating dishes on steam baths. Cold dilute alcohol was added with much stirring and decanted several times. The darkened lime salts thus obtained were taken up in water and decolorized with animal charcoal. On repetition of the above process the lime salts became granular in appearance and so free from sugar that 0.5 g. showed no reduction with Fehling's solution. The air-dried lime salts weighed 60.7 g. and on ignition 0.3978 g. of calcium salts gave 0.0718 g. or 18.05% calcium oxide.

The calcium was split off by treating the lime salts in a hot dilute solution with a slight excess of oxalic acid. After filtering, the aqueous solution was distilled under reduced pressure, as usual, and the residue dried. The thin syrupy acids which weighed 40.5 g. dissolved, with the exception of 0.3 g., in 500 cc. hot absolute alcohol. This solution was concentrated several times and set aside in the ice box, but no crystals formed. Finally it was concentrated to a weight of 80 g., representing 40 g. of gums and 40 g. of alcohol. There were now added slowly 250 cc. of absolute ether with much shaking and the whole mixture placed in the ice box over night. On decanting the ether solution and distilling, 30.9 g. mobile light brown residue, Fraction A, was obtained. The portion insoluble in absolute ether was darker and thicker and weighed 9.1 g. To the latter was added acetic ether in repeated portions of 300 cc. each, and the mixture refluxed till no more of the gum went into solution. The acetic ether solution was concentrated and set away but no crystals formed. Finally the ether was removed by distillation and 8 g. of gum, Fraction B, obtained. The remaining gum, Fraction C, soluble in absolute alcohol weighed 0.9716 g.

Fraction A.—On standing for some time after careful drying, the entire ether residue weighing 30.9 g., solidified to a homogeneous mass of leafy crystals characteristic of glycollic acid. Its identity with this acid was established in five different ways.

The melting point of the crystals was found to be 80°.[1]

[1] Nef, *Ann.*, **357**, 223.

A portion was carefully dried in a vacuum desiccator, weighed and dissolved in water. A part of this solution, equivalent to 0.2678 g. of crystals, on titration required 34.72 cc. of 0.1 N sodium hydroxide, or 64.8 cc. for 0.5 g. The theoretical amount required for 0.5 g. of glycollic acid is 65.8 cc.

To 4.1 g. of A was added 4 cc. 50% alcohol and 7.09 g. of phenyl hydrazine. After standing three or four days at room temperature the mixture suddenly became a mass of fine crystals. These were filtered off and recrystallized twice from 30% alcohol. Three and one-tenth grams of shiny hexagonal plates with a melting point of 100°[1] were obtained.

Four and six-tenths grams of the crystals from the residue A were digested eight hours on a boiling water bath with 5 g. of quicklime. An excess of 5 g. of calcium hydroxide was filtered off. On concentration of the filtrate, 3.4 g. of crystals of calcium glycollate were obtained and recrystallized. 1.0100 g. of air-dried salt lost on drying to constant weight at 100° to 120° 0.2838 g. of water.

<div align="center">Calculated for $Ca(C_2H_3O_3)_2$ $4H_2O$ H_2O, 27 48; found, 28 09</div>

The remaining 0.7266 g. of anhydrous calcium salt gave on heating 0.2126 g. of CaO.

<div align="center">Calculated for $Ca(C_2H_3O_3)_2 \cdot$ CaO, 29 47; found, 29 27</div>

Four and five-tenths grams of the residue A on being treated with an excess of strychnine in the usual manner gave on crystallization 8.0 g. strychnine glycollate melting at 185° to 190°.[2]

On heating the strychnine glycollate with an excess of quicklime for ten hours there was obtained 3.4 g. of calcium salt. 1.2125 g. of air-dried salt lost on being dried in the air bath to constant weight as above 0.3420 g. of water.

<div align="center">Calculated for $Ca(C_2H_3O_3)_2.H_2O$. H_2O, 27.48; found, 28 20.</div>

The remaining salt, 0.8705 g., gave on further heating 0.2550 g. of CaO.

<div align="center">Calculated for $Ca(C_2H_3O_3)_2$: CaO, 29 47; found, 29 29</div>

Fraction B.—This residue of 8.0 g. was diluted with water to 250 cc. Ten cc. of this solution containing 0.32 g. of the original gum was diluted to 100 cc. and treated with 49.8 cc. of 0.1 N sodium hydroxide. This was heated for ten minutes on the boiling water bath and the excess of sodium hydroxide titrated with 0.1 N hydrochloric acid. A total of 23.19 cc. 0.1 N sodium hydroxide was thus used to neutralize 0.32 g. of the acid. On the basis of this titration, the calculated amount of brucine, 25.5 g., was added to the acid solution, together with a small amount of alcohol.

[1] *Ann.*, **357**, 233.

[2] Nef, *Ibid.*, **357**, 238.

This was digested on the boiling water bath one hour after the complete solution of the brucine. On concentrating the solution under reduced pressure a white precipitate of 5.1 g. formed which was filtered off and proved to be brucine.[1] The water was removed by distillation and the residue taken up in half its weight of water and five times its weight of absolute alcohol, after which seven crops of crystals, totalling 20 g., were obtained as follows: 5 g., 1.9 g., 1.5 g. and 1 g. of transparent plates, melting respectively at 198–202°, 195–202°, 202–205° and 190°; 8 g., 1.6 g. and 1 g. of small cubes all melting at 175°.

Fraction C.—This alcohol-soluble residue of 0.9716 g. was diluted with water to 100 cc. and titrated as above. Ten cc. of the solution required 7.25 cc. of 0.1 N sodium hydroxide. To the remaining solution was added the calculated amount of brucine, 2.85 g. On taking up the salts in alcohol 0.2 g. melting at 184° and 0.2 g. melting at 185° crystallized out. After concentration a residue of 1.5 g. was left which, combined with a corresponding residue from Gum B, made 9.5 g. In order to convert this combined residue into free brucine and acid, sodium hydroxide was added on the basis of one and one-half molecules of sodium hydroxide to one molecule of the brucine salt of an assumed four-carbon atom acid. Eight grams of brucine were filtered off. To neutralize the sodium hydroxide a slight excess of hydrochloric acid was added and the solution distilled to dryness. The salty residue was dissolved in water and redistilled to remove all traces of hydrogen chloride. The acid was then taken up in absolute alcohol and, after the removal of the alcohol, 2.052 g. of gum were obtained. This residue was titrated as before in a 2% solution and 0.5 g. was found to require 38.49 cc. 0.1 N sodium hydroxide.

The remaining portion of the solution was digested eight hours on the boiling water bath with 3.3 g. of quicklime. The filtrate on standing gave 0.7869 g. of crystals. On heating these to a constant weight 0.7245 g. was obtained. After ignition 0.1702 g., or 10.85%, of calcium oxide was left.

The high melting salts, including the first four crops from B and the two small crops from C, were combined, making 9.8 g. in all. Likewise the remaining low melting salts from B were combined, making 10.6 g. On treatment with sodium hydroxide in the usual way the high melting salts gave 2.4 g. of acid gum and the low melting salts 3.2 g. On standing, after having been freed from absolute alcohol by distillation, the low melting salts gave 0.52 g. of leafy crystals resembling in appearance glycollic acid and melting at 79°. This was boiled with strychnine, and after filtering off the excess gave, on concentration, 0.2 g. of strychnine glycollate crystals melting at 185°. The remainder of the solution of this residue was added to a similar residue from the high melting salts.

[1] Anderson, *Am. Chem. J.*, **42**, 410 (foot-note) (1909).

The 2.4 g. of gum from the low melting salts, on being taken up in alcohol and allowed to stand for some time, gave 0.32 g. of the characteristic crystals of mannonic lactone melting at 150°. Some of this was mixed with pure mannonic lactone with no change in melting point.

After various futile attempts at identification, the remaining portion from the low melting salts was combined with that from the high melting salts, giving 2.32 g. An optical determination of the latter gave: $d =$ 1.054; $p = 2$; $i.$ $e.$, 0.5223 g. substance and 25.5927 g. water; $[\alpha]$ in a 1 dcm. tube equals —0.70°; whence $[\alpha]_D^{20} = $ —33.2°.[1] Of the residual gum 0.5 g. was found to require 37.55 cc. 0.1 N sodium hydroxide. With quicklime the final portion gave 0.8364 g. air-dried, calcium salt. This, on drying to constant weight, lost 0.0886 g. or 10.5% water. On ignition 0.1271 g., or 17% of CaO was obtained.

Summary.

1. Saccharinic acid formation does not take place at room temperature when maltose is treated with an alkaline solution of hydrogen peroxide with an alkalinity of 0.43 N.

2. The ratio and nature of the oxidation products from maltose with alkaline peroxide are quite different from that of glucose with the same reagent, a fact which must be attributed to the effect of the glucosido bond.

3. Approximately half of the maltose in the reaction mixture used, oxidizes as such. The remainder is apparently hydrolyzed before oxidation.

4. The formation of glucosido acids in the oxidation of maltose explains why a molecule of dextrose requires 2.48 atoms of oxygen by Fehling's solution while the larger maltose molecule requires but 2.86 atoms with the same reagent.

5. The formation of α- and β-d-isosaccharinic acids from maltose under the influence of mild alkalies involves free hydroxyl groups on the first, second and third carbon atoms from the free aldehyde group. These carbon atoms are therefore eliminated as having taken part in the glucosido bond.

6. The formation of relatively large amounts of γ-d-glucosidoglycollic acid in the oxidation of maltose rather than γ-d-glucosidoglycerinic acid indicates that the terminal or primary alcohol carbon atom functions in the glucosido union of the two d-glucose molecules which go to make up maltose.

7. The formula of maltose is that of a γ-d-glucosido-d-glucose with the glucosido union on the primary alcohol carbon.

8. It is probable that maltose under the influence of alkalies enters into an equilibrium of the six glucosido-hexoses of the glucose series, the

[1] Glattfeld, *Am. Chem. J.*, **50**, 150.

dissociation and oxidation of whose intermediate hexose-dienols result in the various oxidation products found.

This work was originally undertaken under the mistaken impression that it was part of certain problems on sugar oxidations granted by Dr. Nef to one of us (Lewis) in 1909. The investigation was well under way before the error, fully acknowledged here, was discovered. The results are now published, however, with the full consent of Dr. Nef, grateful recognition of whose generosity in the matter is herewith freely accorded.

The oxidation products of Fehling's solution on maltose and on lactose are now being studied in this laboratory and, with their completion, the authors will discontinue, as requested by Dr. Nef, all research on the oxidation products of the sugars with inorganic reagents.

BRAIN CEPHALIN: I. DISTRIBUTION OF THE NITROGENOUS HYDROLYSIS PRODUCTS OF CEPHALIN.

By C. G. MacArthur.

The constitution of cephalin is uncertain. Though the nature of the glycerophosphoric acid produced on hydrolysis is fairly well established,[1] the nitrogenous substances[2] and the fatty acids[3] present are not definitely known either as to identity or quantity. This series of investigations was started three years ago in an attempt to clear up these two uncertainties in the cephalin molecule.

This paper considers the preparation of cephalin, the methods used in determining quantitatively its various nitrogenous products and the data obtained by these methods.

Preparation and Purification.—Fresh sheep brains were cleaned carefully, ground in a meat grinder with a small amount of thymol, spread in very thin layers on glass plates, and placed in an air drier. By frequent turning the tissue dried in a day. The dry material was scraped off and placed in a vacuum desiccator. In some cases, instead of the above air-drying method, the dehydration was accomplished by adding to the tissue twice its weight of alcohol or acetone and filtering after a day's standing.

After complete desiccation the cholesterol was extracted by continuously shaking the tissue with twice its weight of acetone. Two such treatments of about four hours each removed practically all the cholesterol.

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[1] Dimitz, *Biochem. Z.*, **21**, 337.

[2] Thudicum, "Die chemische Konstitution des Gehirns," p. 142; Koch, *Z physiol. Chem.*, **36**, 134; Neubauer and Frankel, *Biochem. Z.*, **21**, 321.

[3] Cousin, *J. pharm. chim.*, **24**, 101 and **25**, 177; Dimitz and Frankel, *Biochem. Z.*, **21**, 337; Parnas, *Biochem. Z.*, **22**, 411.

The cholesterol-free tissue was then similarly treated with benzene. This removed most of the phosphatids, among them cephalin.

After concentrating the benzene solution the cephalin was precipitated by very slowly adding it to twice the volume of absolute alcohol. The precipitate was evacuated and dried in a calcium chloride desiccator. On dissolving this material in ether, freshly distilled over calcium chloride, an insoluble substance remained. Because it cannot be satisfactorily filtered or centrifuged, it was separated by allowing the ether to stand in tall cylinders in an ice-box. The clear liquid was siphoned off, concentrated in a vacuum and reprecipitated by alcohol, then dried as before. This process of solution in ether and precipitation with alcohol or acetone was repeated until no insoluble material remained. The final product was a yellow-white powder which will be called cephalin (o).

Several different procedures were used to further purify the various preparations of cephalin. One lot was emulsified in water, filtered and precipitated by a slight excess of hydrochloric acid. To separate thoroughly, the liquid was centrifuged and the precipitate washed by the same process. The procedure was repeated and the substance then dried in a vacuum desiccator. On powdering, a brownish yellow, slightly sticky, hydroscopic material resulted. This will be referred to as cephalin (1).

In purifying another preparation, the watery emulsion was salted out by sodium sulfate, the precipitate washed, and the process repeated. Finally the cephalin was dissolved in ether, precipitated with acetone and evacuated. This product had a similar appearance to that of (1). This will be called cephalin (2).

Another method used was to shake the watery emulsion in a separatory funnel with redistilled ether. The ether layer was dehydrated with anhydrous sodium sulfate and precipitated with acetone. After a repetition of this process and a desiccation of the product it was slightly darker than either of the first two preparations; it will be designated as cephalin (3).

The method least open to objection is a reprecipitation of the ether or benzene or petroleum ether solution a large number of times by alcohol or acetone. The solvent is changed each time, as is also the precipitating agent. A better and more rapid purification is obtained by adding the solution slowly with continuous stirring to the alcohol or acetone. This cephalin is a light, yellowish white, hydroscopic powder (4).

By choosing an amount of alcohol (95%) or acetone not quite sufficient to produce a complete precipitation, a partial separation of the more soluble cephalin occurs. One lot of cephalin (4) which had been precipitated three times was put through this partial separation. The first four fractions remaining dissolved were united and carefully evaporated to a light brownish, waxy, non-powderable material, to be called cephalin

(5). The next four fractions were treated similarly, but gave a yellow, hard, powderable preparation (6). The residue which had been precipitated twelve times was brittle, light brown, and not sticky. This should be very pure cephalin. It will be referred to as preparation (7).

These seven products differed but little in their nitrogen and phosphorus content. Many nitrogen analyses gave an average of 1 60%. The phosphorus was never far from 3 65%.

Quantitative Methods and Data.—After trying out the various acids and alkalies used for hydrolysis, it was found that the best results were obtained with 1% hydrochloric acid. Three grams of cephalin were hydrolyzed by boiling for twenty hours, cooled and filtered. The nitrogen in the fatty acid residue was determined by the usual combustion method and called *residue nitrogen.* The filtrate, after careful evaporation to dryness, was repeatedly extracted with absolute alcohol The insoluble material contained nitrogen as ammonium chloride. This was determined and labeled *alcohol-insoluble nitrogen.* The alcohol solution was precipitated by alcoholic chloroplatinic acid This precipitate was found to be ammonium chloroplatinate, and so the nitrogen in it, when added to the alcohol-insoluble nitrogen, would be *ammonia nitrogen* To distinguish between these two determinations, the nitrogen in the platinum precipitate will be labeled *platinum nitrogen.* After removing the excess of platinum by hydrogen sulphide the above filtrate was evaporated to dryness and taken up in water. It was made slightly alkaline with sodium carbonate and mercuric acetate was added as long as a precipitate formed while keeping the solution alkaline with the sodium carbonate [1] An equal volume of alcohol was added and the solution filtered. The nitrogen in the precipitate was labeled *mercury precipitate nitrogen*, that in the filtrate *mercury filtrate nitrogen* The precipitate has been found to be amino acid and amino alcohol, the filtrate mostly amino alcohol,[2] the latter being but partly precipitated as the mercury compound. Two of many analyses by this method follow

	Impure cephalin (0)	Cephalin (1)
Residue nitrogen	0 53	0 25
Alcohol-insoluble nitrogen	0 05 } 0 20	0 11 } 0 25 ammonia nitrogen
Platinum nitrogen	0 15	0 14
Mercury precipitate nitrogen	0 66	0 89
Mercury filtrate nitrogen	0 15	0 22
Total nitrogen	1 54	1 51

Many attempts were made to reduce the amount of nitrogen in the residue. Seventy-five hours' hydrolysis in dilute acid or alkali did not

[1] Neuberg and Kerb, *Biochem Z*, **40**, 498

[2] A later publication of this series describes the finding of these two compounds See also Bauman, *Biochem Z*, **54**, 30 for the finding of amino alcohol

lower it, nor did twenty hours in 10% sulfuric acid or 10% potassium hydroxide. It was not reduced by alcoholic hydrochloric acid. It seems to be a constant quantity of any preparation of cephalin. During purification the amount is lowered to a definite limit, beyond which further treatment does not reduce it. An unpurified cephalin (o) gave 0.53% residue nitrogen, but after purification, as cephalin (2), this became 0.28%. Results of a similar nature have been obtained for brain lecithin, heart cuorin, and heart lecithin.[1] All give a part of the nitrogen in the residue.

Another method of studying the nitrogen distribution was worked out which was found more satisfactory than the above. After the hydrolysis of the cephalin in 1% hydrochloric acid for twenty hours the fatty acids were filtered off and the filtrate very slowly and carefully evaporated to dryness. The residue was taken up in water made slightly alkaline with potassium carbonate or hydroxide, and air passed several hours to drive off the ammonia, which was collected in standard acid.[2] The solution was then made slightly acid with hydrochloric acid and carefully evaporated to dryness, taken up in water and made to 25 cc. in a measuring flask. In 10 cc. the total amino nitrogen was estimated by the amino apparatus.[3] A 5 cc. portion was used for the determination of the amino acid nitrogen by the copper method.[4] The nitrogen in the other 10 cc. was estimated by combustion. This gives the total nitrogen in the filtrate from the fatty acids and is a control on the total amino nitrogen. Several typical analyses by this method are given below:

	Cephalin (4). Per cent.	Cephalin (7).	
		Per cent.	Per cent.
Residue nitrogen	0.21	0.25	0.27
Ammonia nitrogen	0.21	0.22	0.21
Amino acid nitrogen	0.39	0.70	0 73
Amino alcohol nitrogen (by diff.)	0 79	0 40	0 40
Total amino nitrogen	1.18	1.10	1.13
Total filtrate nitrogen	1.20	(1 18)	1.18
Total nitrogen	1.60	1.57	1.61

In this table it will be noticed that the residue nitrogen, the ammonia nitrogen, and the total amino nitrogen are nearly constant in the different preparations, but that the amounts of amino acid and amino alcohol nitrogen vary largely. To find out whether this might not be due to cephalin being a mixture, an attempt was made to partially separate the two fractions. This was done as described above for the preparations

[1] See a later article for data. See MacLean, *Biochem. J.*, 4, 38 and 240.
[2] Denis, *J. Biol. Chem.*, 8, 427.
[3] Van Slyke, *Ibid.*, 12, 275.
[4] Kober, THIS JOURNAL, 35, 1546.

of cephalins (5), (6), (7). It will be seen from the accompanying table that the amino alcohol content is larger in the more soluble portions, while the amino acid increases in the more insoluble part.

	Cephalin (0, 4). Per cent	Cephalin (5) Per cent	Cephalin (6) Per cent	Cephalin (7). Per cent.
Amino alcohol nitrogen	0 82	0 82 •	0 87	0 38
Amino acid nitrogen	0 32	0 25	0 22	0 74

Cephalin (0, 4) is a sample partially purified according to the cephalin (4) method. It was probably similar to the preparation from which cephalins (5), (6) and (7) were derived.

With the purification of cephalin (7) the per cent. of amino acid constantly increased. After the first treatment there was 0 46% nitrogen in this form. Later in the process this became 0 64% and finally 0 73%. This last value is not a final one. It simply indicates the extent of the separation.

Conclusions.

It may be concluded from the above data that:

1. There is neither choline nor neurine in cephalin.

2. Cephalin has its nitrogen in four forms. These are residual nitrogen, about 0 20%; ammonia nitrogen, about 0 20%; amino alcohol nitrogen, 0 80%; and amino acid nitrogen, 0 40%. These are values for a typical pure product.

3. Ordinary cephalin is probably made up of at least two cephalins, one containing a large percentage of all its nitrogen as amino alcohol, the other having the larger amount of its nitrogen as amino acid.

I wish to express my indebtedness to the late Waldemar Koch for his suggestion of this line of work and for his valuable advice during the first months of the investigation. I am also indebted to Professor A. P. Matthews for suggestions during the progress of this work.

LABORATORIES OF BIO-CHEMISTRY OF THE
UNIVERSITIES OF CHICAGO AND ILLINOIS.

[CHEMICAL SECTION, IOWA AGRICULTURAL EXPERIMENT STATION]

CHEMICAL CHANGES DURING SILAGE FORMATION.

BY RAY E. NEIDIG
Received September 4, 1914

Introductory.

Studies on the volatile aliphatic acids and the lactic acid in corn silage have been reported in previous publications.[1] It was shown that both nonvolatile and volatile acids are present in considerable amount, and occur in the ratio of about four parts of the former to three of the latter. The principle volatile acids were acetic and propionic, these being pres-

[1] Dox and Neidig, *Iowa Agr. Exp. Sta Research Bulletins* 7 and 10.

acid in the proportion of about ten to one. The nonvolatile acid was found to be lactic acid. In the three types of silos examined very little difference was noted in the above ratios.

The results, thus far reported, deal principally with the composition of silage at various periods subsequent to the fermentation. The uniformity of the successive samples throughout the feeding season seems to indicate that whatever changes occur after the early period of silage formation are of only minor importance. Chemical changes taking place during the fermentation period were not discussed at any length in the previous reports. It is known, of course, that the freshly cut corn contains soluble sugars and very little acid, whereas the silage made from it contains considerably less sugar but an abundance of acid. It is reasonable to assume, therefore, that the acidity of silage is developed at the expense of the sugar. The mechanism of the process has not, however, been satisfactorily explained. Babcock and Russell,[1] of Wisconsin, attribute the formation of silage mainly to intramolecular respiration of the green plant cells and regard bacterial activities as only of secondary importance. Russell,[2] of Rothamstead, and Hart and Willaman,[3] of Wisconsin, still maintain this view. On the other hand, Esten and Mason[4] find yeasts and lactic acid bacteria in silage in such enormous numbers that their chemical activities cannot be disregarded.

It is already known that the acidity of silage practically reaches its maximum in less than three weeks. Esten and Mason observed a still more rapid fermentation, most of the acid having developed in the first seven days, with only a slight increase thereafter. It is evident, therefore, in order to follow the chemical changes that constitute silage formation, samples must be examined at frequent intervals during the two weeks immediately following the time of filling the silo. The work described in this paper represents a series of observations made upon the contents of three distinct types of silos during the actual process of the silage formation.

Investigations upon the hollow clay tile silo and the wooden silo were conducted in the fall of 1912. These silos have been described in the work already mentioned. The third, a concrete silo of monolithic type, is forty feet high and fourteen feet in diameter. Investigations on this silo were conducted during the fall of 1913.

Methods.

The determinations made upon the fermenting silage include the following: reducing sugars both before and after inversion, volatile acid,

[1] Babcock and Russell, *Wisconsin Annual Report*, 1900.

[2] Russell, *J. Agr. Sci.*, **2**, 392–410

[3] Hart and Williman, THIS JOURNAL, **34**, 1619–25.

[4] Esten and Mason, *Storrs Agr. Exp. Sta. Bull.* No. 70.

lactic acid, alcohol, and analyses of the gas from the interior of the silo. Temperatures of the silage were also taken in the silos   As in the previous work, the samples of silage were taken by means of an auger, subjected to a pressure of 350 kg per sq cm and the juice thus obtained was used for the analytical determinations

Determination of Sugar —To 100 g of the juice, 15 cc of a solution of neutral lead acetate were added the volume made up to 250 cc and the solution filtered   Of the filtrate 200 cc were treated with just sufficient anhydrous sodium carbonate to precipitate the lead and the solution again filtered   Duplicate portions of 25 cc of this filtrate were used for the sugar determinations by Allihn's method   For the determination of reducing sugars after inversion 50 cc of the lead free solution were mixed with 5 cc concentrated hydrochloric acid allowed to stand 24 hours then neutralized and diluted to 100 cc   The reducing sugar in 25 cc of this solution was determined as above   Cuprous oxide was weighed directly and calculated as glucose in both cases

Determination of Volatile Acids —Volatile acids were determined by the Duclaux method as in the method cited [1]   The Duclaux fractionation was made upon one half of the solution, after removal of the barium sulfate instead of first distilling into two fractions and making separate titrations and calculations   On account of the great preponderance of acetic acid, very little is accomplished by this preliminary fractionation, while the calculation is rendered still more laborious

Determination of Lactic Acid —After removing the volatile acids by distilling with steam under reduced pressure, lactic acid was determined, as in the previous work, by extracting the residue with ether and crystallizing out the zinc salt   Observations were then taken with the polariscope to determine the optical activity and the zinc salt was identified by determining the percentage of zinc oxide present.

Determination of Alcohol —100 g of the silage juice were neutralized with sodium hydroxide, transferred to a 200 cc distilling flask and distilled from a glycerol bath   The volume of the distillate collected in each case was 75 cc   This was diluted to 100 cc and 50 cc were transferred to a 300 cc flask and boiled for 15 hrs under a reflux condenser with 5 g chromic acid and 5 cc concentrated sulfuric acid   The volatile acids resulting from the oxidation of the alcohols were distilled with steam until a distillate of 1 liter was collected   This was titrated with 0 1 N barium hydroxide using phenolphthalein as an indicator   The acid was calculated as acetic acid and recalculated to ethyl alcohol

Gas Analysis —A brief description of the apparatus used for obtaining samples of gas from the interior of the silo will be given here   A one-half inch galvanized pipe was inserted vertically from the bottom of the silo, at the center, extending to a height of about ten feet   At the upper end, a two-foot piece of one-inch pipe containing numerous small holes was attached   The lower end was extended along the floor and up the side to a height of about six feet and then protruded through the wall, a stopcock being fitted to the end   The entire length of pipe was given

[1] *Research Bulletin* No 7, Iowa Agr Exp Station

a thin coat of shellac on the inside. The purpose of inserting the pipe vertically from the bottom of the silo was to prevent any interference with the normal settling of the silage. The above described apparatus was installed in the three silos, constructed of hollow clay tile, wooden staves, and concrete, before filling.

Samples of gas, representing in each case the gas from the center of the silo at a height of about twelve feet from the bottom were obtained by means of an aspirator.

The analysis was made in an Orsatt gas apparatus. 100 cc. of the gas were measured into the buret, then transferred to the pipet containing the potash solution (1 part KOH to 2 parts H_2O) and allowed to remain there ten minutes, the operation being repeated in order to insure complete absorption of the carbon dioxide. The gas was then transferred to the buret and the decrease in volume noted. This decrease represents carbon dioxide. The contents of the buret were now transferred to the pipet containing alkaline pyrogallol solution (1 part 25% pyrogallol solution to 6 parts 60% KOH) and subjected to the same manipulation as before. The loss in volume represents percentage of oxygen. The residual gas consists chiefly of nitrogen.

Temperature Observations.—The apparatus used in obtaining the temperature of different parts of each silo at frequent intervals consisted of a portable indicator and twelve electric thermometers, each connected with 15 feet of insulated wire. Four of the thermometers were buried in each silo at the time of filling, about fifteen feet from the top. The position of the thermometers in each silo was the same; one at the center, one at the outside edge next to the silo wall, and the remaining two on a direct line with the two former thermometers in such a position that they were equidistant from each other and the center and outside thermometers. When readings were desired each thermometer was connected with the indicator and on passing an electric current through the apparatus, the temperatures were read directly in degrees Fahrenheit on the indicator scale. The temperature observations on the wooden stave and hollow clay tile silos were taken a year later than the chemical studies on these two silos, yet, for the sake of comparison, they are included in this paper.

Experimental.

Wooden Stave Silo.—The wooden stave silo was filled Sept. 23, 1912, with Reed's yellow dent corn. The stalks were somewhat green and the corn well dented in the ear. Water was added to the top of the silo immediately after filling. The analytical results are shown in Table I.

Hollow Clay Tile Silo.—The hollow clay tile silo was filled September 27, 1912. The corn was Reed's yellow dent, somewhat riper in appearance and contained less moisture than that put in the wooden stave silo. No water was added to this silo. The first sample was taken on the day of filling and represents the fresh corn juice. Samples 2 and 3 were taken Sept. 28 and 29, respectively. Owing to the small amounts

TABLE I.

Nr. of sample.	Age of sample (days).	Per cent of moisture in silage.	Acetic acid, g.	Propionic acid, g.	Butyric acid, g.	Valeric acid, g.	Total volatile acid, g.	Lactic acid, g.	Sugars calculated as glucose. Before inversion.	After inversion.	Alcohol,[1] g.	Per cent of CO₂.	Per cent of oxygen.
1	0	76.3	Volatile and non-volatile acids were not						2.570	5.1960	0.01	1.4	18.0
2	1	73.0	separated in the first two samples.						3.680	4.5160	0.16	45.0	1.0
3	2	67.6	0.4178	0.0166	0.0039	0.0044	0.4427	0.7565	2.574	2.7840	0.39	66.4	1.4
4	3	65.1	0.5152	0.0374	0.0000	0.0000	0.5526	0.8807	1.760	1.7600	0.32	68.0	0.5
5	4	66.0	0.5090	0.0476	0.0000	0.0000	0.5566	0.6404	2.018		0.29	52.0	0.0
6	5	64.7	0.5348	0.0444	0.0000	0.0000	0.5792	0.6560	2.050		0.25	50.0	0.0
7	6	66.5	0.5624	0.0446	0.0000	0.0000	0.6070	0.7698	2.436	Determinations discontinued.	0.20	55.0	0.0
8	7	67.6	0.6482	0.0448	0.0000	0.0000	0.6930	1.0070	1.842		0.30	55.0	0.0
9	8	67.5	0.5976	0.0414	0.0000	0.0000	0.6390	0.5680	1.796		0.31	55.0	0.0
10	9	65.3	0.7488	0.0520	0.0000	0.0000	0.8008	1.2270	1.438		0.48	56.0	0.0
11	10	68.3	0.5182	0.0538	0.0000	0.0000	0.5720	0.9857	2.046		0.19	46.0	0.0
12	11	67.2	0.5598	0.0698	0.0000	0.0000	0.6296	1.0020	2.144		0.24	33.8	0.0
13	17	65.6	0.5890	0.0612	0.0000	0.0000	0.6502	1.6170	1.305		0.37	32.4	trace
14	23	65.2	0.5932	0.0726	0.0000	0.0000	0.6658	1.4980	1.218		0.31	32.7	trace

[1] Calculated as ethyl alcohol.

of acidity, the volatile acids were not determined by the Duclaux method in these samples but simply calculated as acetic acid. The analytical results follow:

TABLE II.

No of sample.	Age of sample (days).	Per cent of moisture in silage.	Acetic acid, g.	Propionic acid, g.	Butyric acid, g.	Valeric acid, g.	Total volatile acid, g.	Lactic acid, g.	Sugars calculated as glucose. Before inversion.	After inversion.	Alcohol,[1] g.	Per cent of CO₂.	Per cent of oxygen.
1	0	64.3	Volatile acids were not sep-				0.0310[2]	0.160	2.552	4.590	0.02	26.7	1.6
2	1	62.0	arated in the first three				0.1080[2]	0.287	4.970	5.292	0.07	41.0	0.0
3	2	65.5	samples.				0.1170[2]	0.224	4.493	4.754	0.11	48.0	0.0
4	3	64.0	0.1472	0.0092	0.0017	0.002	0.1601	0.342	4.334	4.726	0.17	58.0	0.0
5	4	57.9	0.2700	0.0281	0.0000	0.000	0.2981	0.289	3.254	3.378	0.20	48.0	0.0
6	5	63.1	0.3400	0.0392	0.0000	0.000	0.3792	0.544	3.248	3.264	0.26	50.0	0.0
7	6	61.2	0.3416	0.0354	0.0000	0.000	0.3770	0.569	2.840	Determinations discontinued.	0.30	48.0	0.0
8	7	58.8	0.4026	0.0419	0.0000	0.0000	0.4445	0.799	2.260		0.30	46.0	0.0
9	8	60.9	0.4182	0.0436	0.0000	0.000	0.4618	0.646	2.280		0.29	40.0	0.0
10	10	63.4	0.3972	0.0458	0.0000	0.000	0.4430	0.921	1.640		0.38	35.4	trace
11	12	62.3	0.4742	0.0578	0.0000	0.000	0.5320	1.108	1.050		0.46	31.1	0.0
12	19	58.5	0.5048	0.0524	0.0000	0.000	0.5572	1.340	1.226		0.41	27.2	0.0

[1] Calculated as ethyl alcohol.
[2] Calculated as acetic acid.

Concrete Silo.—The concrete silo was filled September 15, 1913, with Reed's yellow dent corn. The corn was well dented and quite dry owing to a lack of rain previous to filling the silo. Water was added to the top of the silo on the morning of September 20th. After thoroughly soaking the top of the silage oats were sown, which soon sprouted and formed a thick matted covering over the surface of the silage. No separation of the volatile acids by the Duclaux method was made from the samples of silage from this silo. The total volatile acids were calculated as acetic acid. The analytical results are shown in Tables III to VI.

TABLE III

No. of sample	Age of sample (days)	Per cent of moisture in silage	Total volatile acid,[1] g	Lactic acid, g	Sugars calculated as glucose		Alcohol,[2] g	Per cent of CO₂	Per cent of oxygen
					Before inversion	After inversion			
1	0	59 0	0 0144	0 0000	4 852	9 038	0 02	63 0	1 0
2	1	60 5	0 0426	trace	7 411	8 942	0 20	73 0	0 0
3	2	61 2	0 1914	0 2930	7 406	8 184	0 26	87 0	0 0
4	3	58 6	0 2802	0 5094	6 859	7 089	0 24	80 5	0 0
5	4	60 3	0 3948	0 6264	6 899	7 004	0 19	82 5	0 0
6	5	62 0	0 4812	0 7436	5 506	5 573	0 30	75 0	0 0
7	6	61 7	0 5680	0 9750	4 373	Determinations discontinued	0 22	68 0	0 0
8	7	63 4	0 6060	1 0115	4 070		0 27	66 0	0 0
9	8	63 3	0 6660	1 3452	3 206		0 38	65 0	0 0
10	10	64 5	0 7032	1 1719	3 370		0 30	56 0	0 0
11	14	65 5	0 7176	1 2356	2 736		0 33	54 0	0 0
12	21	65 6	0 7368	1 4053	2 558		0 37	40 5	0 0

[1] Calculated as acetic acid
[2] Calculated as ethyl alcohol.

Discussion.

Before taking up the discussion of the results obtained from the foregoing investigation on silage formation in the three types of silos, a few preliminary remarks concerning the scope of the work are given for the benefit of the reader. Several factors enter into the work which exert a decided influence upon the amounts of chemical products formed in the silo and therefore must be reckoned with in the discussion of the results. Two of the chief factors are the maturity and moisture content of the corn. It is known that, the more immature the corn, the greater the amount of acid produced. Differences in maturity also show differences in the sugar and moisture content and, as acids are formed chiefly at the expense of the sugars, it is evident that any differences in the maturity of the corn would materially effect the quantities of the chemical products. Since the three silos were not filled with corn of uniform maturity and water

was added to two of the silos, the results will not be compared quantitatively but the general ratio of the chemical products will be used for the basis of the discussion and the merits of the three types of silos discussed from this viewpoint.

A comparison of the sugar determinations shows that in each case the juice from the green plant contains about equal amounts of reducing sugar and non-reducing sugar. The latter may be considered sucrose. During the first two days after filling the silo, the most noticeable change is the inversion of the sucrose. When the sugar determinations before and after inversion coincided, the inversion was considered complete and no further determinations were deemed necessary. The rate of inversion was not the same in the three silos, the wooden silo requiring three days, the hollow-clay tile silo four and the concrete silo five days. No significance, however, can be attached to these differences, inasmuch as the chemical changes vary at the same rate. The inversion of sucrose is probably due, to the greater extent, to the enzyme sucrase. Acids, likewise, bring about the hydrolysis of sucrose, but their effect in this instance is prac-

TABLE IV —TEMPERATURE READINGS.

Wooden Stave Silo Filled Sept 13, 1913

			Readings of thermometers placed			
		at center	two feet from			Temperature of
Date of reading	Time of reading	Degrees Fahrenheit	center Degrees F	wall Degrees F	at wall Degrees F	atmosphere Degrees F
Sept 13[1]	8 00 A M	80	80		76	..
Sept 14	7 00 A M	80	77		66	
Sept 15	7 00 A M	77	77		65	
Sept 16	7 45 A M	76	76	87	74	65
Sept 17	7 00 A M	76	76	87	70	65
Sept 18	7 00 A M	78	78	87	66	
Sept 19	8 00 A M	78	78	87	66	64
Sept 20	7 45 A M	80	80	87	60	48
Sept 21	7 45 A M	80	80	87	54	43
Sept 22	8 30 A M	81	81	86	47	47
Sept 23	7 30 A M	81	81	86	56	49
Sept 24	7 30 A M	82	82	86	66	66
Sept. 25	7 45 A M	83	82	84	58	49
Sept 26	7 45 A M	83	82	83	48	45
Sept 27	2 00 P M	84	83	83	60	72
Sept 28	5 15 P.M	84	83	82	61	60
Sept 29	5 00 P M	84	83	82	66	65
Sept 30	4 45 P M	84	84	81	66	70
Oct. 1	5 00 P M	85	84	81	68	76
Oct 2	3 30 P.M	85	84	80	66	76
Oct 3	2 30 P M	86	84	80	68	83
Oct 4	2 40 P.M	86	84	80	63	66
Oct 6	11 30 A M.	85	84	79	67	81

[1] Water was turned on top of silo at 8 30 P M and allowed to flow all night.

tically negligible for the reason that organic acids are weak catalysers and, at this early period of silage formation, are present only in small amounts. Although it is not possible to state the exact source of the enzyme, sucrase is known to be present in the corn plant itself, and it is also a product of numerous microörganisms including bacteria, yeasts and molds.

From the time of filling the silo the total sugar decreases in amount, until a minimum is reached in about three weeks. In the case of the hollow tile silo this minimum was reached in twelve days. In no instance does the reducing sugar disappear completely. Even after a much longer period the presence of reducing sugars can be demonstrated. A sample of silage juice, 120 days old, from the concrete silo, was found to contain 3.1 g. reducing sugar per 100 g. juice. In order to identify the sugar, a portion of the juice was clarified with neutral lead acetate in the usual manner, concentrated on the water bath, and then treated with phenylhydrazine hydrochloride and sodium acetate in a flask immersed in boiling water. After a few minutes yellow crystals separated from the hot solution. These were filtered out and washed with cold water, then recrystallized five times from 50% alcohol. The substance showed a melting point of 204–206°. Phenylglucosazone melts at 205°. From

TABLE V.—TEMPERATURE READINGS.

Hollow Tile Silo Filled Sept. 18, 1913.

| | | | Readings of thermometers placed | | | |
| | | | two feet from | | | Temperature of atmosphere. Degrees F. |
Date of reading.	Time of reading	at center. Degrees Fahrenheit.	center. Degrees F.	wall. Degrees F.	at wall Degrees F.	
Sept. 18	1.00 P.M.	77	78	79	66	..
Sept. 19	8.00 A.M.	81	82	83	64	64
Sept. 20	7.45 A.M.	83	85	85	60	48
Sept. 21	7.15 A.M.	85	86	86	52	43
Sept. 22	8.30 A.M.	86	87	87	47	47
Sept. 23	7.30 A.M.	87	88	88	54	49
Sept. 24	7.30 A.M.	88	89	89	66	66
Sept. 25	7.45 A.M.	88	90	89	57	49
Sept. 26	7.45 A.M.	90	90	90	50	45
Sept. 27	2 00 P.M.	90	91	90	58	72
Sept. 28	5.15 P.M.	90	91	89	61	60
Sept. 29	5.00 P.M.	90	91	88	64	65
Sept. 30	4.45 P.M.	90	91	88	64	70
Oct. 1	5.00 P.M.	90	91	88	68	76
Oct. 2	3.30 P.M.	90	91	87	64	76
Oct. 3	2.30 P.M.	90	91	87	66	83
Oct. 4	2.40 P.M.	90	91	86	68	66
Oct. 6	11.30 A.M.	90	90	85	67	81
Oct. 7	5.00 P.M.	90	90	85	64	70
Oct. 8	5.15 P.M.	90	90	85	66	70
Oct. 10	4.30 P.M.	90	90	84	65	57

the melting point, the insolubility in hot water, and the crystalline form of the osazone, it is evident that the sugar was either glucose or fructose, or a mixture of the two. Examination of the clear sugar solution in a polariscope showed dextro rotation, indicating therefore, that the sugar consisted of glucose either in the pure state or greatly in excess of the fructose.

The results on the acidity of silage show that in each case there is a gradual rise in volatile acids. In the two silos, wooden stave and hollow clay tile, the individual volatile acids were determined and approximately the same proportions of propionic to acetic acid was found as noted in the previous publications on this subject.[1] Butyric and valeric acid were found to occur in traces only in one sample from the wooden silo. The three silos show differences in the rate of formation and the maximum yield of volatile acids, but this cannot be attributed to the different types of silos. The ratio of volatile acids to lactic acid is approximately a constant for the three silos. Lactic acid was found to increase in the concrete silo similar in manner to the wooden and hollow clay tile silos. The samples of zinc lactate examined in a polariscope proved to be the racemic.

TABLE VI.—TEMPERATURE READINGS.

Concrete Silo.[2]

| Date of reading. | Time of reading. | at center Degrees Fahrenheit. | Readings of thermometers placed two feet from | | at wall Degrees F. | Temperature of atmosphere Degrees F. |
			center.	wall Degrees F.		
Sept. 16	7.00 P.M.	80		80	70	70
Sept. 17	7.00 A.M.	82		81	68	65
Sept. 18	7.00 A.M.	84		84	68	..
Sept. 19	8.00 A.M.	86		85	65	64
Sept. 20	7.45 A.M.	86		86	60	48
Sept. 21	7.15 A.M.	88		87	54	43
Sept. 22	8.30 A.M.	88		87	48	47
Sept. 23	7.30 A.M.	88		89	52	49
Sept. 24	7 30 A.M.	88		89	64	66
Sept. 25	7.45 A.M.	90		88	58	49
Sept. 26	7.45 A.M.	90	Thermometer short-circuited.	88	52	45
Sept. 27	2.00 P.M.	90		87	55	72
Sept. 28	5.15 P.M.	90		87	59	60
Sept. 29	5.00 P.M.	90		88	62	65
Sept. 30	4.45 P.M.	90		88	62	70
Oct. 1	5.00 P.M.	90		86	64.	76
Oct. 2	3.30 P.M.	90		86	60	76
Oct. 3	2.30 P.M.	91		85	62	83
Oct. 4	2.40 P.M.	91		85	67	66
Oct. 6	11.30 A.M.	91		84	67	81
Oct. 7	5.00 P.M.	90		84	64	70

[1] Loc. cit.
[2] Filled Sept. 16, 1913.

or inactive variety. While the maximum yield of lactic acid and volatile acids varied for the three silos, no significance can be attached to these differences, since factors which would influence the chemical changes in silage were noticed at the time of filling the silos, such as the moisture content and the maturity of the corn.

The alcohols found in silage were calculated as ethyl alcohol; although it is known that other alcohols are formed in small amounts during silage formation. The tables giving the results for the hollow clay tile and concrete silos show a gradual increase in the amount of alcohol, while the results for the wooden silo indicate that the amount of alcohol found on the third day after filling the silo is almost equal to the maximum amount observed during the period of investigation for this silo. It is further noted that the results on this silo are quite irregular and do not follow any gradual increase as in the case of the hollow clay tile or concrete silos. The alcohol found probably owes its origin, in the greater part, to yeasts, since these are known to be present in enormous quantities at the beginning of silage formation. It is difficult to state with the present evidence whether or not alcohol occurs as a transitory product. It is quite probable, however, that a small part of the acetic acid which is found in silage is the result of oxidation of some of the alcohol. The mechanism of this reaction cannot be definitely explained as yet, since free oxygen is absent from the interior of the silo except in traces. It is possible, however, that microörganisms are an aid in this oxidation.

The gas analyses on the three silos show practically the same results: carbon dioxide is formed very rapidly during the first few days, and after reaching a maximum, which differs slightly for each silo, gradually decreases until a minimum of approximately 20% of the entire gas is reached. Oxygen, on the other hand, disappears entirely during the first few days. The residual gas consists mainly of nitrogen, a considerable amount of which must gain access to the silo from the top. As air diffuses downward the nitrogen replaces the carbon dioxide and accumulates while the atmospheric oxygen is used by the aerobic bacteria and fungi found at the surface of every silo. This, it appears, satisfactorily explains the presence of two or three feet of spoiled silage always found at the top of silos.

The temperature observations on the three silos were taken every eight hours during the early period of silage formation. Since no appreciable differences were observed during these short periods, only the temperatures taken twenty-four hours apart are given in the foregoing tables. The question of the temperatures attained in the silo during the early period of silage formation is one which is very much in dispute and it is hoped that the results obtained will greatly aid in clearing some of the erroneous conceptions commonly held. As the silage in each of the

three silos was pronounced by experts to be in excellent condition, it is only reasonable to suppose that the observed temperatures are the actual temperatures prevailing during the formation of good normal silage.

It is well known that higher temperatures are reached at the top of the silos where oxygen gains entrance and partially spoiled silage results. Similarly, if oxygen gained access to the silage, due to insufficient settling of the silage or to faulty construction of the silo, higher temperatures would be noted. In the author's opinion, a great number of the conflicting statements found in the literature on the temperatures observed in silos can be directly attributed to the factors just mentioned.

The results on the three silos during the period of examination indicate that no importance can be attached to the superiority of any one type of silo over others in regard to the conductivity of heat through the silo walls. It was intended to continue the temperature observations throughout the winter, with a view of ascertaining the relative conductivity of the silo walls, but since the silage was fed below the depth of the thermometers before cold weather, this point could not be determined and is, therefore, reserved until a future date. However, it is quite probable that the three silos will show similar properties.

The chemical changes occurring during the early period of silage formation are very similar in the rate of formation and the quantity of the chemical constituents produced. When the fact is taken into consideration that the corn was in a different state of maturity when put into the different silos, it is not surprising that such results are obtained and they can hardly be attributed to differences in the types of silo.

A complete study of the bacterial flora of silage is necessary, in the author's opinion, before definite statements can be made upon the causes of silage formation. It is hoped that these results on the chemical changes in silage may be an aid in such an investigation.

Conclusions.

The results show that no differences, which could be attributed to the effect of different types of building materials upon the process of silage formation, were noted in the chemical changes of the silage in the three silos. It is readily seen that approximately the same results are obtained in the temperature observations, gas analyses and determinations of alcohol, sugars, and the volatile and nonvolatile acids of the silage from the three silos. The only differences noted are the differences in quantity; the ratio of the chemical substances, however, is very nearly the same for each silo.

The question now arises as to the comparative value of the silage. Is silage of high acidity of more value than that of low acidity? In the author's opinion silage must have a sufficient amount of acidity to insure its keeping, but beyond this point additional acid is neither essential

nor beneficial. A large amount of acid is known to be harmful but the quantity which gives the maximum food value has not been determined.

Remarks Concerning the Value of Different Types of Silos.

Since the three silos produced excellent silage, a short discussion of the relative value of the different types of silo will be included in this work. In the past the main argument used by wooden silo manufacturers was the superiority of wood over stone, brick, hollow tile, or concrete as a material for the silo walls. They based their conclusions upon the fact that wood is less a conductor of heat than the other materials. The temperature results on the three types of silos show that little stress can be laid on this point, as all three silos showed relatively the same temperatures. The results also show that a high temperature is not an essential factor in the production of good silage, since the maximum temperature noted in the three silos was 91° Fahrenheit. Moreover, the period of silage formation is of short duration, about three weeks at the most, and it occurs at a time of the year when the weather is not exceedingly cold, hence for this reason alone, conductivity of the silo wall would not play an important part in silage formation. As for silage freezing in severe cold weather in the silos, the writer has failed to notice any advantage in using any one particular material for the silo walls, as the three silos, constructed of wooden staves, hollow tile, and concrete, respectively, froze approximately the same amount in each instance. Much stress has also been laid concerning the effect of the acids upon the stone, hollow tile and concrete walls which results in forming a portion of spoiled silage next to the walls. The writer believes that such instances are due either to the walls not being air-tight, thus allowing air to gain access to the silage, or to rough surface walls, which prevent the thorough settling of the silage near the walls. Examination of the concrete and hollow tile silos, which have smooth walls and contained silage which was properly packed failed to show any spoiled silage. The chief factors necessary for the production of good silage are, therefore, smooth, air-tight walls, corn in the right state of maturity, the proper amount of moisture, and carefulness in filling. These four factors properly carried out will insure a good quality of silage with a minimum loss due to spoiled silage.

Summary.

Examination of the contents of the three types of silo in use at the Iowa Agricultural Experiment Station showed the following chemical changes during the actual period of silage formation:

1. Nonreducing sugars was rapidly changed to reducing sugar, and the latter then decreased in amount but did not disappear completely.

2. The amount of volatile acids increased daily.

3. In the concrete silo, as already demonstrated for the hollow tile and

wooden stave silos, the racemic lactic acid produced showed a daily increase.

4. Alcohol was formed in small amounts in each silo.

5. Carbon dioxide developed very rapidly after filling the silo.

6. Free oxygen disappeared entirely after the second or third day.

7. The maximum temperature observed in any of the three silos was 91° Fahrenheit.

8. Within the limits of this investigation, no differences were noted which might be attributed to differences in the material of which the silos were constructed.

AMES, IOWA.

NEW BOOKS.

General Chemistry: Part I, **Principles and Applications,** pp. vi + 410; Part II, *Experiments*, pp. xiv + 174. By LYMAN C. NEWELL. Boston· D. C Heath & Co. 1914. Price, $1.20 (separately, Part I, $1.00; Part II, 60 cents.)

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The order of topics chosen seems to result in frequent mention of subjects not yet discussed. Nitric acid, with its numerous reduction prod-

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Introduction to Organic Chemistry. By JOHN TAPPAN STODDARD, Professor of
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pp. viii + 469. Price, $1 50.

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principles of organic chemistry and its relations to general chemistry.

* * * * * Emphasis is laid on general reactions and characteristics, rather than on special facts relating to particular compounds. * * * * * * Many applications of organic chemistry to practical life are given. * * * * * The book is considerably smaller than many of the texts on the subject, but it is believed that it is none the less complete in all the essential matter which is properly presented in a first course."

In the opinion of the reviewer the author has been fairly successful in his efforts. The size and scope of the book reminds one of Remsen's "Organic Chemistry," although the method of presentation is somewhat different.

It has seemed to the reviewer that the text, in common with a number of texts in organic chemistry, is unnecessarily cold and uninviting for a first course. The great number of acts to be presented and the desire to keep the text within ordinary limits naturally lead to the omission of much interesting information. Perhaps it is the intention of the author that such information should be supplied by the teacher—but unfortunately this expectation is not always realized. The author of the text, before us uses no illustrations or figures of any kind, unless indeed one considers structural formula as falling under this head. Of course illustrations and pictures are not necessary in such books—neither are they in our homes for that matter; but if properly selected they may in either case have an educational value.

The author makes the statement that formaldehyde is used as a food preservative and gives the well-known method for detecting its presence in milk. The reviewer doubts if this compound is any longer used for this purpose. He also doubts if 95% alcohol can be made for 20 cents a gallon.

On the whole, the book contains the fundamental principles of organic chemistry presented in a fairly attractive way and may be recommended to teachers in search of such a text. WM. McPHERSON.

Elementary Household Chemistry: An introductory text-book for students of Home Economics. By JOHN FERGUSON SNELL, Professor of Chemistry, MacDonald College, McGill University. New York. The MacMillan Company 1914. pp. 307. Price, $1.25.

The task which the author has set for himself in these pages is, in the nature of the case, a difficult and, as it seems to the writer of this review, an undesirable one. The title page says it is an introductory text-book for students of home economics. The field of home economics covers many subjects and is fairly well outlined for study under the divisions of food, clothing and shelter. Even in the present undeveloped stage of the subject, there is abundant material for an elementary book upon any one of these divisions. Moreover, it is to be hoped that the student

of elementary household instruction is not taking up home economics, dietetics and dyeing even in the same year. If, as the preface states, "The text has been written with the needs in mind of students the majority of whom have had no previous instruction in chemistry," the writer doubts if this is a good way to teach either chemistry or home economics. Further, if, as the preface states later, the author had also in mind "the needs of students who had had training in general chemistry," then it seems such students ought to be able to use a less elementary book, to be ready to do more intensive work in both chemistry and some one phase of home economics. In other words, in the present stage of development of home economics, even elementary work in it requires elementary knowledge of four rather than one science.

While the reviewer has little sympathy with this method of teaching either elementary chemistry or home economics, she does find much excellent material in the book. The subject matter is put in an interesting and clear way. Much ingenuity has been shown in selecting the experiments, in the elimination of irrelevant matter, and in the presentation of the essentials.

The following suggestions are offered concerning the experiments. If one wished to prepare carbon dioxide (p. 5), it would seem that it could be done more easily and more simply, and when grape sugar and yeast are used, it would be better to take a liter flask and a cake of yeast, and then test for other products as well as carbon dioxide; again, strenuous objection is made to testing temperature by the hand (p. 7); chemistry applied to the household ought to teach accuracy by the use of scales and the thermometer and neither of these instruments are suggested in this text; the statements (p. 181) concerning jelly-making do not agree with the results of Miss Goldthwaite's investigations; it seems desirable if one teaches any classification of proteins (p. 184) to use the one agreed upon by scientists; the amount of flour used in making the gluten test (p. 190) is far too small for satisfactory results, and it is most desirable to obtain the gluten from the flour of both soft and hard wheats in order to enable the student to learn that fundamental distinction in flours.

The appendix contains much useful material well arranged. A good bibliography adds greatly to the value of the text. The book will be helpful to the student of elementary chemistry and may provide suggestions and illustrations for teachers of home economics in secondary schools.

ISABEL BEVIER.

T.W. Richards

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THE PRESENT ASPECT OF THE HYPOTHESIS OF COMPRESSIBLE ATOMS.[1]

By Theodore W. Richards

Speculation concerning the ultimate nature of the material Universe goes far back into the early history of mankind. As soon as several of the ancient Greek philosophers perceived that some kind of atomic hypothesis is the simplest method of accounting for things, they attempted to imagine the nature of the ultimate particles. The apparent permanence of the Universe suggested that these particles could never become worn out, and hence the ancients naively conceived of them as being infinitely hard. Newton inherited this idea, and speaks more than once of "hard, massy particles." Not much over a hundred years ago, Dalton brought forth convincing quantitative evidence in favor of the atomic theory, putting it thus upon a firm basis and the theory was later adopted by physicists to explain the pressure of gases. Throughout these considerations the notion of hard, incompressible (but perfectly resilient) atoms persisted, partly because this assumption served as a convenient basis for mathematical analysis.

According to the tenets generally held during the last fifty years, solids and liquids, as well as gases, are supposed to be constituted of small hard

atoms (or complexes of hard atoms called molecules) with wide, empty spaces between them—these particles being supposed to be each for itself in violent irregular motion to and fro, due to heat. There is, however, nothing in this philosophy to distinguish solids and liquids from gases, although in reality they are very different indeed. Such a conception gives a very reasonable picture of the state of a gas, but does not explain the fixed bulk of liquids nor the rigidity and impermeability of solids To overcome these difficulties, it was necessary, in discussing solids and liquids, to add to the hard imaginary incompressible particle a magic "sphere of influence" surrounding it, which would prevent its touching other atoms; but how this "sphere of influence" was constituted no one was quite prepared to say.

About fifteen years ago, in studying the behavior of gases, I came to the conclusion that, even with this dilute form of matter, the imaginary particles (although here widely separated) were still surrounded by "spheres of influence," somewhat but not very much larger than those imagined to exist in liquids. This conclusion raised a serious question as to the real boundary of the space occupied by the atom itself. It seemed that since a "sphere of influence" appears always to accompany the atom, the little hard particle in the middle might have no real physical significance; this imaginary hard particle appeared to be a purely arbitrary assumption. The so-called "sphere of influence" in all its relations acts as if it were really the important thing to be considered. Hence the question was proposed· Why should we not call this "sphere of influence" the atom itself, since it always accompanies the atom; why should we pretend to know anything about how the material is distributed within its limits? The gain in this point of view is twofold. In the first place it concentrates the interest and attention upon the entity which actually comes into consideration; on the other hand, it abolishes an arbitrary hypothesis. Moreover, since the so-called "sphere of influence" appears to be rarely spherical, even the designation of the old idea is of doubtful legitimacy.

If then, we consider this space which the atom actually occupies in liquids and solids as being the bulk of the atom, we must admit that the atom is compressible; for this space is diminished by increasing pressure. In other words, liquids and solids are actually compressed when pressure is applied to them.

Such atoms, compressible and elastic throughout their substance, would be capable of sustaining and transmitting heat-vibration, even if closely packed together; hence this conception of solids and liquids does not interfere with the mechanical conception of heat.

One can easily see that the new hypothesis is suggestive. If atoms are compressible, and are packed closely together in solids and

may we not trace, through the alteration in bulk of substances during chemical change, the action of the chemical and cohesive affinities which hold the atoms together? May we not with the help of this study interpret anew the mysterious symmetry of crystals? May we not correlate numerous properties in relation to one another and by means of the fundamental conception show the mutual dependence of all the properties of matter?

In this brief address I shall not attempt to present all the far-reaching applications of the theory of compressible atoms, but I shall endeavor to show how the new conception explains many apparent inconsistencies in the earlier interpretation, and how it presents the picture of the manifold phenomena of the physico-chemical Universe in a new and more reasonable light. In so far as is possible in a brief presentation, the endeavor will be made to discuss systematically the most important applications of the theory which have thus far been made. Let us begin with the properties of gases, which, as I have said, first suggested the idea.

To the layman, the attempt to discover anything whatever from the properties of gases as to the spaces occupied by molecules themselves might at first seem quite hopeless, for everyone agrees that in gases (at least under ordinary pressure) there must be wide, empty spaces between the molecules, so that the total bulk occupied by the gas as a whole must be made up of the sum of the comparatively small space actually occupied by the molecules and the much greater spaces between them.

The task would indeed be hopeless except for the existence of the well-known, simple laws of Boyle (or Mariotte) and Charles (or Gay-Lussac) governing gases. These laws, we have every reason to believe, should apply with absolute precision to a perfect gas—an abstraction which may be defined for the present purpose as a gas in which the molecules are imagined as mathematical points without any attractive affinities. They tell us, as you well know, that the volume of a perfect gas ought to be exactly proportional to the absolute temperature, and inversely proportional to pressure. If these laws apply exactly to the imaginary case in which the molecules occupy no space whatever, it is evident that any deviation from them ought to afford a clue as to the actual bulk occupied by the molecules in any given gas. This aspect of the question was first pointed out by Budde in 1874; and three years afterwards, van der Waals saw clearly, for the first time, that not only the bulk occupied by the molecules, but also the attractive affinities between them must affect the volume of a gas. This latter agency would diminish the outward pressure (and, therefore, the volume under constant pressure) by pulling the particles inward. Taking account of these two tendencies, namely, the tendency of the molecule itself to occupy space and its tendency to attract other molecules, van der Waals constructed his well-known equation, which

modifies the simple gas-law by making a definite allowance for both,
$(p + a/v^2)(v - b) = nRT.$

Now it is well known that nobody has ever been able to find for any gas a perfectly constant quantity (b) which will serve in this equation to represent (for all temperatures and pressures) the exact amount of space occupied by the molecules themselves. Fifteen years ago, this inadequacy in van der Waals' equation excited my interest, and I sought to discover, if possible, the reason for the lack of the exact fulfilment of the mathematical expression. The matter is complicated by the coëxistence of the two effects mentioned in the preceding paragraph; it is difficult to be sure that the affinity-effects have been entirely eliminated from the estimate of the bulk. Nevertheless, careful study made it seem highly probable that at least one reason for the inconsistency is simply a real changeableness in the space occupied by the molecules under varying circumstances.

In other words, it seemed as if the molecules sometimes occupy more space and sometimes less, as if they might be diminished in bulk by pressure (in other words, compressed), and as if they might be affected in size also by changing the temperature.

At that time, however, although the results were suggestive and led to a search for signs of atomic compressibility among other phenomena, they did not seem to be conclusive, for two reasons· In the first place one could not be sure, as already stated, that the effect of affinity had been entirely allowed for, and in the next place one could not feel sure whether the compression affected the atoms themselves, or only molecules built of several atoms. In order to obtain conclusive evidence on these points, one must study some gas which has only a single atom in each molecule, and which has practically no cohesive tendency. In such a gas any change in the calculated bulk of the molecules must be referred directly to the atoms, because here in this special case the molecule and the atom are identical; and the lack of cohesiveness or self-affinity would eliminate the complication affecting the pressure, thus going back to Budde's original idea.

Fortunately just such a gas exists in helium, and the recent data of Kamerlingh-Onnes show indeed that helium atoms in all probability change their apparent bulk with changing conditions.[1] One can easily compute the quantity b (which must be a function of the apparent collision-bulk[2] of the molecules) from these data; thus it is found that at 0° C. the quantity b is 12 cc., and at 100° C. it is only 10.4 cc. per 4 g. of helium under moderate pressure.

[1] Richards, This Journal, **36**, 617 (1914).

[2] The apparent collision-bulk is the bulk which is made up of imaginary spheres with the radius of half the apparent distance between atomic centers on nearest approach during collision. It includes an effect due to the time of collision.

Evidently, then, the apparent collision-bulk of the molecules in helium must be smaller at high temperatures than at low temperatures, and the only satisfactory way of accounting for this is to suppose that the greater velocity of the colliding atoms at high temperatures produces a greater compressing effect upon them, so that at high temperatures they seem to occupy less space than at low temperatures. The data are not as plentiful as one would like, but the laboratory work seems to have been carefully done by the great Dutch experimenter, and the evidence is strong. If the helium atoms are thus capable of compression, it is only fair to assume that other atoms are also compressible; and one is given immediately an adequate and satisfactory qualitative explanation for the deviations of all gases from the exact requirements of the equations of van der Waals. If the molecules and atoms are compressible, of course no constant value could be found for their bulk under varying conditions.

Not only the equation of van der Waals, but also that of corresponding states (a mathematical deduction evolved from the former equation) has its difficulties of interpretation smoothed away by this assumption of atomic compressibility. The reason why this equation also is by no means exact, applying only with similar substances, is made clear.

But these interesting conclusions are not the only outcomes of this discussion, for the idea that atoms are compressible at once leads to the conviction that the atoms in gases are much larger than van der Waals supposed them to be. All his conclusions referred to the apparent collision bulk, which must needs (in compressible atoms) be considerably smaller than the true bulk, because of the great velocity with which the colliding molecules in a gas are known to strike one another. Those who are interested will find the argument rather fully set forth in the recent article already mentioned; there is no time here to go into detail, but the outcome may be stated. This is, that the bulk of the molecules, when not compressed, may perhaps be about that of the so-called critical volume. This idea gives us a new definition of the critical point—one of the most puzzling phenomena concerning the relations of liquids and vapors.

The study of the critical point brings us naturally to the next heading of the discourse, namely, the application of this idea of atomic compressibility to liquids and solids. It has just been pointed out that the logical discussion of the properties of aeriform matter indicates that the bulk of the uncompressed molecules in gases is much larger than had previously been expected. Indeed, as stated above, it appears that the actual bulk of the molecule in a gas is to be considered as about the critical volume, which is of course considerably larger than the space occupied by the liquid under ordinary conditions. That is to say, we must imagine the atoms in a liquid as being not only packed closely together, but packed so closely that every atom is much compressed by the force of the cohesion.

This seems revolutionary indeed. 'It was formerly thought that the atoms, even in liquids, were as far apart, relatively to their size, as the planets in the solar system. Van der Waals, to be sure, did away with this extreme view by his equation, giving good evidence that the atoms were at least as large as one-third of the space occupied by the liquid; but the new conception now advocated makes them much larger still.

In what direction must we seek for further evidence of the close-packing and compression of atoms in liquids and solids? Much is at hand. Striking support for this hypothesis is seen in the slight contraction which liquids and solids suffer on being cooled to the absolute zero. If the atoms really have wide spaces between them in solids, these spaces should disappear at the absolute zero, where heat-energy is supposed no longer to exist; but no substance known to me contracts anything like as much on cooling to very low temperatures as it should to correspond with the requirements even of van der Waals' theory.[1] Evidently something very different from heat vibration is the chief tendency which maintains the bulk of liquids and solids.

Precisely in line with this conclusion is the inference to be drawn from the compressibility of matter at low temperatures. If the ordinary conception of matter is true, it should be wholly incompressible at the absolute zero; on the other hand, if the theory of compressible atoms is true, matter should be almost as compressible at the absolute zero as it is at ordinary temperatures. I pointed out in the Faraday Lecture of 1911 that the latter is probably the case, basing the conclusion on an extrapolation of the results of Grüneisen obtained at very low temperatures. In this crucial case again the facts decide in favor of the theory of compressible atoms.

Yet another obvious argument among many may be cited. The ordinary theory demands that all material should be porous with large spaces between actively moving molecules. This idea is so interwoven in the science of today that most text-books on physics name porosity as one of the universal properties of matter. Now as a matter of fact in very many cases porosity is conspicuous by its absence. Liquid has been imprisoned in quartz and other materials for countless ages; many solids indeed (especially crystals) are thoroughly impervious both to liquids and to gases. This could hardly be the case if there were wide spaces between the rapidly moving molecules. Other instances are cited in the Faraday Lecture of 1911, to which those interested may be referred.

That an occasional substance, such as monoclinic sulfur which has been metamorphosed into the rhombic form at low temperatures, or iron (which undergoes a well-recognized solid transition below its melting point), or amorphous fused silica, might have minute pores within its fabric is only to be expected; this fact does not militate at all against the theory.

[1] THIS JOURNAL, 36, 626 (1914).

From another point of view also, the ordinary conception of a solid has always seemed to me little short of an absurdity. A gas, indeed, may very properly be imagined as consisting of moving particles independent and far apart from one another, but how can a rigid solid like steel possess such an unstable structure?

These and many other considerations, then, lead me to conclude that in solids and liquids not only are the atoms packed closely together to form molecules, but that also these molecules are packed closely together to form the material solid and liquid substances which we can see and handle. We must conclude that heat vibration occurs in these closely packed molecules by a somewhat different mechanism from the rectilinear motion which we all imagine to be the carrier of heat energy in gases. We must imagine that these compressible molecules are working upon one another in somewhat the fashion discernible in the microscope among small floating particles and called the "Brownian movements." Of course, the molecular upheavals must take place on a much smaller scale, but the analogy is illuminating. Such a motion would obviously turn into a rectilinear one if a molecule were freed from its bondage to other molecules, that is to say, vaporized.

Having thus step by step come to the conclusion that the atoms in liquids and solids must be packed closely together and that they must be compressed in this close contact by the forces which hold them together, we are immediately stimulated to study in detail the effect which cohesion and chemical affinity may have on these compressible objects, the atoms. May not the study of the changes exhibited by the volumes of liquids and solids under varying conditions be able to throw much light on the forces which hold solids and liquids together if all this be true?

Chemical affinity and cohesion are phenomena of the utmost importance in our daily life. The existence and stability of all the complex molecules which make up our bodies and our environment depend upon the chemical affinity; and cohesion is the agency which causes these molecules to assume the solid and liquid states, without which the world would be indeed "without form and void." Therefore, the study of these agencies is highly important to anyone interested in man's relation to the physical universe in which he has been placed.

We know very little about the nature of the forces which produce these effects, and every phenomenon which can throw light upon them should be eagerly pressed into service.

The first question which demands answer before any conclusions can be drawn is the question whether chemical affinity and cohesion exert pressure in their action, or whether they merely hold the atoms and molecules together without pulling them toward one another. I am aware of no adequate discussion concerning this point, important as it is; and I

doubt if there is unanimity among chemists and physicists concerning it. Of course, all know that gravitation, at least, acts at a distance and pulls objects together. When two objects are in contact, gravitation causes their surfaces to press on one another. Undoubtedly gravitation has something to do with cohesion and chemical affinity, but it is equally certain that some agency besides gravitation comes into play. Does this other force or concatenation of forces also pull inward?

Clearly the theory of compressible atoms gives us a means of finding an answer to this question. For if the atoms are compressible, a force which pulls them together will diminish the volume of the system by pressing them upon one another. But a force which merely holds the atoms together, without pulling inward, could have no such effect. Hence, assuming pragmatically that the practicable bulk of an atom is compressible, we may infer that cohesion exerts pressure if we find diminished volume in cases where great cohesion is known to exist. Precisely the same argument may also be applied to chemical affinity. Consistency in the outcome must afford strong support for the assumption on which the inference was based.

Plentiful data exist supporting this point of view. Although it is somewhat difficult in a brief lecture of this sort to present clearly the situation (because the variables are so many that no feasible mode of representation can make all of the relationships clear at once) it is hoped that the following explanation may be comprehensible and convincing:

Let us first study the behavior of cohesion, because some knowledge of cohesion is necessary in order to interpret chemical affinity. Cohesion manifests itself in various ways. The most obvious is the mechanical resistance to the separation of one part of a substance from another. Thus it appears, often modified, in the properties of ductility, malleability, tenacity, hardness, and may be supposed to be concerned with surface tension and with resistance to evaporation. There are, therefore, many guides which afford an approximate idea of the magnitude of the cohesive tendency which may exist in a substance.

We may then ask ourselves: Do bodies having great cohesive affinity act as if they were under great internal pressure? If this is the case, it would not be unreasonable to ascribe the great pressure to great cohesion.

What now are our guides as to the presence of pressure in a given system? The most obvious is the diminution of the volume, because pressure always produces decreased volume. Diminishing volume of course means that the density of the substance in question is increased. Hence, other things being equal, if the external pressure is constant, at least one of the causes of the appearance of a greater density in a given substance may be the existence of a greater internal pressure within it.

Another evidence that pressure exists within a given system is to be found in the slight effect of further additional pressure. From this tentative clue, based upon experience, one may infer that the existence of only a slight compressibility in any system probably signifies the residence already in that substance of considerable internal pressure, upon which the slight added increment will have but little percentage effect.

Yet another still more subtle evidence of great pressure in any system is the constancy of the compressibilities under changing pressure. In a system already under great pressure each small successive addition of pressure will be nearly the same percentage of the whole, and, therefore, each like addition would be expected to have very nearly the same effect upon the volume. On the other hand, if the substance is under small pressure, each successive equal addition of pressure will be a much smaller percentage than the preceding and would, therefore, have a greatly diminished effect upon the volume. Thus if the compressibility decreases greatly with increasing pressure, one may infer that but little pressure was present in the first case, but if a body possesses a small compressibility which is nearly constant over a wide range of pressure, we should feel obliged to believe that a great internal pressure was already present in some form within the substance.

A fourth means of guessing as to the presence of internal pressure may be inferred qualitatively from the effect of temperature upon the body being studied. Where a rise of temperature produces a very marked effect upon the volume, we may guess that there are only gentle forces holding the body together; but where the effect of rising temperature is slight, we may suppose the internal pressure to be great.

We have, then, in addition to the several criteria indicating a tendency to *hold* together, four different methods of evaluating a tendency to *pull* together. If the phenomena show that these tendencies all go hand in hand the presumption would be very strong that great cohesion produces pressure, and that this pressure is actually effective in reducing the volume of solid and liquid substances.

Because of the many variables involved, it is clear that our safest conclusions are to be drawn from the comparison of isomers; here we can compare a number of substances having exactly the same components.

The following table compares seven properties of two typical organic isomers. In every case the relation is exactly in accord with the theory in question. The denser has the less compressibility, the less decrease of compressibility with pressure, the less coefficient of expansion, the higher boiling point, the greater surface tension and the greater heat of vaporization. That this solidarity of all the properties should be due to chance is extremely improbable.

	Ethyl butyrate.	Ethyl isobutyrate.
Density...	0.8785	0.8710
Compressibility $\times 10^6$.............................	76.9	80.8
Decrease of compress. (per 200 atm.) $\times 10^6$....	13.6	13.0
Coeff. of expansion[1]...............................	0.001247	0.001294
Boiling point............................	120.8°	109.8°
Surface tension..........................	24.58	23.3
Heat of vaporization (kilojoules per mol)............	34.7	33 9

Many other such tables might be given; and although in some cases deviations from the theory appear, the percentage of agreement among the many substances which I have thus far compared is so very great that the evidence is overwhelming.

Let us now change our method of comparison. Instead of comparing many properties of two substances, let us compare two properties of many substances. For example let us compare the boiling points and densities of substances having the formula $C_7H_{14}O_2$.[2] Here it is seen that the greater density follows closely the higher boiling point, exactly as the theory suggests. (The diagram is given on the opposite page.)

Again, the comparison of the surface tensions and compressibilities of a number of compounds of carbon, hydrogen, nitrogen, and oxygen chosen at random shows a marked tendency to grouping in a definite curve of the kind predicted.[3] This is very striking, especially when one considers the great variety of substances discussed. The relation between the compressibility and its decrease with pressure is also striking.[4] Here again, although there is some scattering, the points are all grouped near a definite curve, showing that there is a real relation of exactly the sort indicated by the theory of compressible atoms. It is clear that all these phenomena taken together constitute so strong a basis of fact that one can hardly avoid the conviction that they are due to a common cause; and the only reasonable cause seems to be the action of cohesion, which is thus shown to exert pressure.

These considerations led to the actual experimental study of compressibility because, as a rule, it is a mistake for anyone to theorize greatly

[1] These data were determined as follows: The rise of temperature needed to make each liquid expand 3.42% of its original volume (in a calibrated dilatometer allowing for the expansion of the glass) was found by repeated experiments to be 27.2° for the butyrate and 26 2° for the isobutyrate. The initial temperature was 21.5°, and the coefficients are referred to the volume at this temperature. The result is, therefore, the mean value over this range (or about that at 35°) referred to the volume at 21.5°. As comparative results alone are needed, this suffices.

[2] Richards, *Proc Am Acad*, 39, 594 (1904) A somewhat similar comparison is made by W. A. Noyes in his *Organic Chemistry*, p. 368 (1902).

[3] Richards and Mathews, THIS JOURNAL, 30, 11 (1908).

[4] Richards, Stull, Mathews and Speyers, *Ibid.*, 34, 990 (1912).

about a series of phenomena, with which he has not come face to face in the laboratory. This work, as well as much other work conducted in this laboratory, has been generously subsidized by the Carnegie Institution of Washington. The already existing methods for determining compressibility having been found inadequate, a new and convenient method for determining this somewhat elusive property was devised. With the help of this method the compressibilities of about forty elements have been determined at Harvard—only two or three having been known before.

BOILING POINTS AND DENSITIES OF SUBSTANCES $C_7 H_{14} O_2$
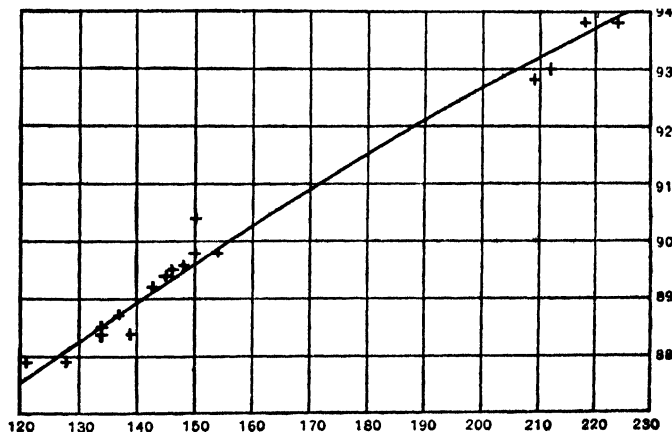
Fig. 1.

The divergent point on the ordinate 150° represents methyl caproate, and that less divergent on the ordinate 139°, isoamyl acetate.

The other substances, named in order, are isopropyl isobutyrate, isopropyl butyrate, propyl isobutyrate, ethyl isovalerate, butyl propionate, propyl butyrate, ethyl valerate, isobutyl propionate, amyl acetate, methyl isobutyl acetate, hexyl formiate, isoamylacetic acid, isoheptylic acid, iso-onanthic acid, and heptylic acid

It was found that in the case of the solid elements the compressibility shows periodic fluctuation as the atomic weight increases, and that in general, with elements as with compounds, the bulky volatile substances are the most easily compressible. This was new—neither the facts nor the explanation had been available before. Obviously the explanation is exactly like that applied to the isomers above. When a substance is held firmly together by cohesion, that is to say, when it is non-volatile, one would expect it to be much compressed by this great cohesion. Therefore, it should be dense, that is to say, have small atomic volume; it should be slightly compressible, and should possess only a small coefficient of expansion. This is precisely the case.

Consistently, elements with great atomic volumes show, in general, also great volatility, great compressibility, great coefficient of expansion, and great change of compressibility with increasing pressure. The accompanying diagram, taken from the Faraday Lecture of 1911, clearly indicates the relation of atomic volume to compressibility in the cases of those solid elements which have been measured.
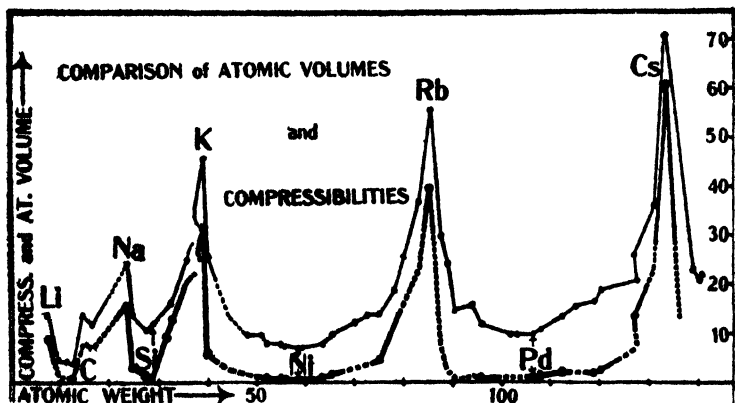
Fig. 2.

It is true that the regularity is not perfect, but the small discrepancies may often, if not always, be explained through taking account of the undoubted fact that the tendency even of elementary atoms to cling to one another manifests itself in diverse ways. Thus many elements make polyatomic molecules, and the internal pressures within the molecule must be greater than those which bind the separate molecules together. This latter cohesive tendency is that which has to do with volatility, whereas the other properties are usually determined by a net effect due to both. On the whole, then, the evidence becomes extremely strong that cohesion exerts pressure.

Let us now turn to chemical affinity.

If cohesion produces compression, must not the far stronger aggregation of forces which (for lack of a better name) we call "chemical affinity" also produce compression? If this is the case, must not chemical affinity be one of the essential factors in determining the volume of all liquid and solid substances? This is a highly important question, the answer to which brings with it quite a new interpretation of the mechanism of chemical action.

Since, as we have seen, cohesion is an important influence in determining liquid and solid volumes, we can only hope to trace the further effect of chemical affinity after we have made allowance for such an effect as

cohesion may produce. Because as a rule both occur together and the total volume must be fixed by superposition of the two effects, it is hard to discriminate between the two. We can, therefore, expect to trace the relative compressing effect of affinity most satisfactorily by comparing cases in which the effects of cohesion in both factors and products are not very different. To cite a definite example, a good case to compare would be the contractions which occur on forming the chlorides of strontium and lead, for the two metals are not very different in boiling point (a fact which shows that their internal cohesive affinity is not very different); moreover, the resulting compounds also are neither of them very volatile; and chlorine is common to each reaction. Hence one may have a reasonable expectation that a comparison of these two substances should yield some clue as to the relative compressing effect of the affinity of chlorine for the two metals.

What are the facts? A gram-atom of strontium occupies 34.5 cc., and two gram-atoms of chlorine occupy 50 cc., or 84.5 cc. in all. But a gram-molecule of strontium chloride occupies only 51.9 cc.; hence in the act of its formation there has been a contraction of 32.6 cc. Similarly, when a gram-atom of lead unites with chlorine there is a contraction of 20.1 cc.; distinctly less than in the former case. This is just what we should expect if affinity causes compression, for the affinity of strontium for chlorine is undoubtedly much greater than that of lead for chlorine. The heats of formation of these chlorides (which in parallel cases of this kind give a roughly approximate idea of the relative free-energy changes involved) are 772 and 346 kilojoules per mol, respectively; moreover, strontium will replace lead in this compound.

Many other similar cases have been noticed from time to time. The first seems to have been pointed out by Humphry Davy in a footnote to one of his papers,[1] and figures of this sort have been quoted occasionally by others (especially Müller-Erzbach Hagemann, and Traube) as showing that high chemical affinity is associated with small volume. Nevertheless none of the earlier observers succeeded in convincing the chemical public of the generality of the proposition, perhaps for the reason that there appeared to be altogether too many exceptions to the rule; moreover, the argument was logically incomplete. According to the present theory, the supposed exceptions are seen, usually if not always, to support the rule; indeed they are really necessary consequences of the rule. The effect of cohesion may entirely mask the effect of affinity, especially when some of the factors or products are volatile substances in which the cohesive internal pressure is slight; again, one must obviously take into account the compressibility of the bodies under examination. Both these modifying tendencies were entirely ignored by the earlier experimenters; but the prob-

[1] Humphry Davy's "Collected Works," 5, 133 (1840).

able influence of each tendency is now clear, and their existence explains many apparent irregularities which are now seen to be due, not to accident, but merely to the necessarily confusing superposition of the several effects.

The example cited above (namely, the comparison of the chlorides of strontium and lead) was especially chosen because the compressibilities of the elements (lead and strontium) are not far apart: the difference in the contraction may therefore be ascribed chiefly to the difference in affinity. The effect of compressibility, on the other hand, is best seen by comparing the contractions occurring during the formation of similar compounds of elements having large and widely different compressibilities, but similar affinities. The series of five alkaline chlorides is especially suitable for this purpose; the elements are all fairly similar to one another as to their cohesiveness (that is to say, their boiling points, except in the case of lithium, are not very far apart) and their affinities for chlorine also are not very different;[1] but their compressibilities vary widely. The following table and diagram compare the latter data with the contraction on combination. It is clear that the greater the compressibility of the metal, the greater is its contraction on combination.

COMPRESSIBILITIES OF METALS OF THE ALKALIES COMPARED WITH THE CONTRACTION OCCURRING DURING THE FORMATION OF THEIR CHLORIDES.

	Compressibilities $(x\ 10^6)$ of elements	Contraction on formation from elements Cc per 1 mol.
Lithium..........................	9.0	17.6
Sodium.........................	15.6	21.5
Potassium........................	31.7	33.1
Rubidium..........	40	36.8
Caesium.	61	53.6

Many comparisons of this sort might be cited, for example, the behavior of the several halides of any single alkali metal is equally striking, but these typical examples indicate sufficiently for a brief discourse the important relation of the compressibilities of the elements to the volumes of their compounds. No more convincing argument in favor of the theory of compressible atoms could be desired.

When the elements entering into such a comparison are widely different in cohesive affinity, or when the resulting compounds are not fairly comparable in this regard, the effect of chemical affinity may be masked by the differences of cohesiveness. Thus the comparison of volatile with non-volatile substances cannot be expected to yield results as consistent as those given above. Enthusiasts or critics interested in the details will find a discussion of typical cases of this kind in previous papers concerning the significance of changing atomic volume.[2]

[1] See the Faraday Lecture of 1911 (Richards), especially the diagram given on page 1215 (*J. Chem. Soc.*, 99, 1201 (1911).

[2] *Proc. Am. Acad.*, 39, 590, 592 (1904); THIS JOURNAL, 31, 190 (1909).
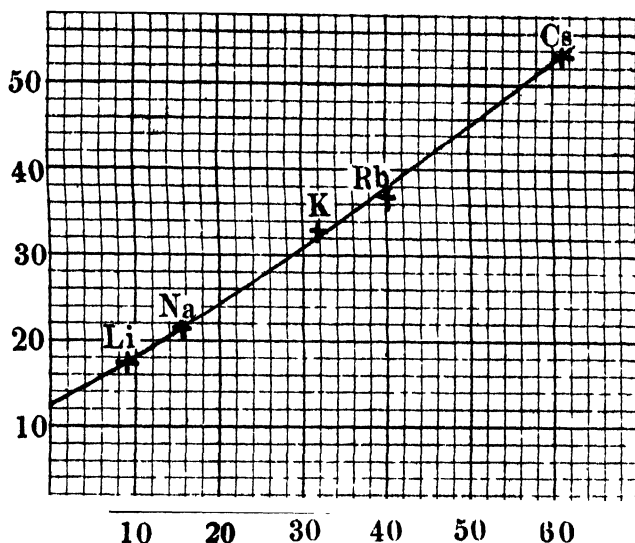
Fig. 3.—Diagram depicting data in table opposite. Contraction on combination (in cc. per mol) is plotted ordinately; compressibilities (of the elements) are plotted as abscissae.[1]

[1] An interesting corollary suggested by this diagram is to be found in the extrapolation of the curve toward the left. The point where the abscissa becomes zero indicates the hypothetical contraction which would take place if an imaginary incompressible element were combined with chlorine by an affinity about equal to that of the others to form a compound similar to lithium chloride. Since, in this case, the contraction of 12.5 cc. must be due to the 25 cc of chlorine alone, we may suppose that in each of the actual cases of the alkali chlorides the contraction must be about the same, and that in each case the chlorine occupies about 25—12 5 = 12 5 cc. From this assumption and the actual total contractions, the table which follows (given here for the first time) has been computed.

APPROXIMATE DETAILED VOLUME-RELATIONS OF SOLID ALKALI CHLORIDES ON THE ASSUMPTION THAT THE CHLORINE IN EACH OCCUPIES ABOUT 12.5 CC.

	Actual total mol vol. of salt	Hypothetical at. vol of metal in salt.	Hypothetical contraction of metal on combination.
Lithium chloride...	20 5	8 0	5 1
Sodium chloride.............	27.2	14 7	9.0
Potassium chloride...........	37.3	24.8	20 6
Rubidium chloride......... ..	44 0	31 5	24 3
Caesium chloride.............	42 4	29 9	41.1

These values do not pretend to be absolutely precise, and their interpretation is complicated by differences in the cohesive properties of the molecules concerned; but they are nevertheless interesting, because they give a clue to the mechanism of the reaction.

The theory has had another interesting outcome, which bids fair to bear much fruit in the future. If atoms are compressible, the uneven compression caused by differently applied chemical affinities might be supposed to restrict the heat-vibration existing within their elastic boundaries. This restriction would lessen their heat capacities (which are measured by the quantities of heat needed to cause a given change of temperature) and, therefore, expel some heat-vibration already present which could no longer be accommodated by the system; for diminished heat capacity at ordinary temperatures probably indicates diminished average heat capacity over the whole range down to the absolute zero.[1]

Since the heat energy contents of any system must be supposed to be represented by the product of the absolute temperature into the integral heat capacity over the whole range (plus the latent heat involved in any change of phase which may have occurred), a diminution of the heat capacity at ordinary temperatures must expel some of this contained heat energy. Thus the theory predicted that, when during a given reaction the heat-capacities of the substances concerned were diminished, one would expect also to find an output of heat during this reaction in excess of that corresponding to the chemical work. Thermal energy thus displaced at constant temperature could not be expected to be capable of doing work; and we may reasonably ascribe to this cause at least a part of the well-known difference between the total-energy change and the free-energy change of an isothermal reaction.[2] Moreover, it seemed probable that some of the driving energy of the reaction might be needed to accomplish this effect, and, therefore, not be able to perform outside work. These two considerations together might account for the puzzling "bound-energy" of chemical change, which was recognized but not explained by thermodynamics. The mathematical analyses of Helmholtz and Lewis (afterwards confirmed by Haber) had shown the problem to be beyond the power of contemporary thermodynamics alone; but the idea seemed so plausible that an effort was immediately made to submit it to practical verification. I was able to show, in cases of certain typical reversible gal-

[1] The somewhat academic theory of the equipartition of energy suggests a difficulty in the situation, demanding that such a system (*i. e.*, one continuously deformable) should possess an infinite heat capacity. But this theorem notoriously fails at low temperatures, and even at high temperatures it is very arbitrary in its assumptions concerning restraints; hence its demands may be set aside in this case. Lack of space forbids here any further discussion of the relative magnitudes of potential and kinetic energy in a condensed system.

[2] Helmholtz had proved that a thermodynamically indeterminate integration-constant was involved in this relation, and Lewis at Harvard had shown mathematically that change of heat capacity must be concerned in "bound-energy:" but neither proposition was sufficiently definite to lead to much outcome. See Haber, "Thermodynamics of Technical Gas Reactions," translated by A. B. Lamb, p. 45, 1911, also G. N. Lewis, *Proc. Am. Acad.*, **35**, 7 (1899).

vanic cells, that when free energy change increases with rising temperature, total energy change decreases, and *vice versa*.[1]

From this interesting discovery two fundamental conclusions were then drawn: first, that "*When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and total-energy changes of the reaction are equal and unchangable with the temperature;*" and secondly, that "*the sign and magnitude of the difference between the free and total energy changes is dependent upon the sign and magnitude of the change of the heat capacity of the system.*"[2] When the heat capacity decreases (as is more usual) during the reaction, the total energy change exceeds the free energy change, and *vice versa*. It was further pointed out that the difference between these two must diminish as the temperature approached the absolute zero, where the two must become identical, running into one another almost if not quite asymptotically.[3] All these ideas were afterward (1906) adopted unchanged by Nernst in his recent development of the "Wärmetheorem" usually named after him.

The next step was obviously to determine the actual amount of heat displaced by change of heat capacity, in order to determine whether or not this was exactly equal to the bound-energy (that is, the difference between the free- and total-energy change). To do this, one must know the specific heats of factors and products over the whole range of temperature; but data were lacking. Hence a new method was devised at Harvard, and the preliminary results showed that the specific heats of solids at low temperatures are much smaller than had been supposed.[4] The intention had been to continue with this highly interesting and significant discovery; but before this could be done, these various ideas also were taken up by Nernst and incorporated into the new "Wärmetheorem."

It is, perhaps, not out of place to point out here that the new feature

[1] That is to say, expressed mathematically $dA/dT = -n\, dU/dT$, in which A represents free energy, U total energy, and n a number, which was found often to be about 2. Of course dU/dT is nothing more nor less than the change of the heat capacity during the reaction. J. M. Bell has questioned the sufficiency of the evidence, but he has neglected to note that although Marignac's data (upon which I relied) were perhaps absolutely not very accurate, they are relatively to one another much more to be depended upon; and in this question relative accuracy alone is concerned (*J. Phys. Chem.*, **9**, 402 (1906)). Bronsted has evidently quite failed to understand the original idea although he has provided much of interest as to its later development (*Z. Phys. Chem.*, **56**, 653 (1906)); but van't Hoff (*Boltzmann Festschrift*, p. 233 (1904)) and Haber (*loc. cit.*) saw its significance

[2] Richards, *Proc. Am. Acad.*, **38**, 307, 300; *Z. physik. Chem.*, **42**, 143, 136 (1902).

[3] This is explicitly stated (*Proc Am. Acad.*, **38**, 301 (1902); *Z. physik. Chem.*, **42**, 138 (1902)). The mathematical expression of the latter alternative (complete tangency) is, of course, that later written by Nernst, namely $(dU/dT)_{T=0} = (dA/dT)_{T=0}$.

[4] Richards and Jackson, *Z. physik. Chem*, **70**, 450 (1909).

first introduced by the mathematical physicist was the arbitrary assumption of the simplified equation $U - \beta T^2 = A + \beta T^2$. This assumption,[1] since abondoned, introduced the great convenience of making the situation amenable to mathematical treatment. Qualitatively the Nernst proposition especially in its recent more complex form, is identical with that older American one from which it was derived; the only essential difference is the assumed quantitative formulation.[2] In 1902 any such attempt at greater definiteness seemed unwarranted by either fact or theory.

In the intervening years, much experimental work has been performed in many laboratories, stimulated by the theorem. So far as I know, all, or nearly all, of these investigations have supported the idea of 1902; but by no means all of them have supported exactly Nernst's later additions to that idea.[3] Nevertheless, the latter has certainly done good service by stimulating research. Moreover, even if the final word upon the groundwork of the theory has not been spoken, the complicated mathematical superstructure reared by Nernst upon the earlier concepts must be conceded to be exceedingly clever and ingenious.

When the exact quantitative statement of the fundamental principle underlying these phenomena is discovered, it will be worthy of ranking with the great laws of thermodynamics; and even now it is possible to make a general statement (like that made in 1902) which may not need revision when the details are mastered, as follows: *Apart from concentration effects, the bound energy change of a chemical reaction is essentially dependent in sign and magnitude upon the change of heat capacity. When the latter is negative the former is positive, and vice versa.*

The theory of compressible atoms was thus the starting point of a long train of thought and experiment.

The suggestion that the idea of atomic compressibility might explain the previously incomprehensible volume changes which occur on dissolving salts in water has recently been discussed by Baxter.[4] He has successfully elucidated, through the comparison of the densities of solutions of alkaline halides, the tendencies at work; and he finds that the facts entirely accord with the predictions of the present theory.

Another suggestive application of the hypothesis concerns the idea of the

[1] See Nernst, "Theoretical Chemistry" (translated by Tizard, p. 712 (Macmillan, 1911)). Later developments have shown the need of more terms; but no attempt will be made here to enter into a discussion of the complex mathematical development of them. Some of the latest curves look very like those published in my early paper of 1902, differing only in details.

[2] Nernst has admitted this identity in one of his American publications. "Thermodynamics and Chemistry," Silliman lectures, p. 56 (1907).

[3] See for example, Naumann, *Z. Elektrochem.*, 16, 778 (1910).

[4] Baxter, THIS JOURNAL, 33, 922 (1911).

"asymmetric" carbon atom of van't Hoff and Le Bel, which is the basis of so much of modern organic chemistry. The observed phenomena are exactly what one would expect if a compressible carbon atom were unequally compressed on four different sides by the four different affinities inherent in four other dissimilar atoms. An atom, spherical in the first place, would thus be compressed into an irregular twisted tetrahedron, which would have its attached atoms securely held on its faces, and not impossibly perched on its projecting angles. Geometrically an arrangement of this new kind answers the requirements as well as the old conception; and it is certainly more plausible from a mechanistic point of view. That such a twisted structure should rotate the plane of polarized light, seems only natural. Moreover, would not the flexible nature of the system make possible just such changes as are manifest in the well-known but not satisfactorily elucidated Walden inversion?

One of the yet more recently developed aspects of the hypothesis is its interpretation of crystal form. The application of the idea to this field was suggested at the beginning; and in two papers which have not long since appeared in our journal, various phenomena exhibited by crystals—such as their definite angles, the similarity of forms assumed by analogous substances, and other details concerning their highly symmetrical shapes—are all accounted for in a fashion which seems (at least to the author) to be more satisfactory than any other thus far suggested. It has long been assumed by most speculators upon the chemical mechanism of crystallization that the spheres of influence of the atoms must be closely packed; but usually these "spheres" are assumed to remain spherical, or nearly so. The present theory greatly modifies this notion by pointing out that the so-called spheres of influence (the atoms themselves, according to the present definition) must be greatly distorted by the affinity exerted in the act of their combination. Thus the atoms must be more closely compacted in some directions than in others. The total result of the crystal-unit or solid molecule thus formed must be a definitely constituted aggregate of closely tied atoms; and the shape in which this crystallographic unit can best fit together with others must determine the crystal form. Specific cases have been worked out with this idea in mind; and the conception has shown itself to be consistent with the known facts of crystallography.[1]

We may well ask: what is the distending tendency, which prevents the affinities of the atoms from contracting all solids and liquids into a mathematical point? I have found it convenient to speak of the boundary of this distending or repelling tendency as the surface of the atom, because it seems to accompany the atom wherever it goes. The present investigation does not attempt to decide how the atom may be constituted within;

[1] THIS JOURNAL, **35**, 382 (1913); **36**, 1686 (1914).

it seeks simply to study and draw inferences from its outward behavior.

Let us review the essential characteristics of the boundary of this distending effect which surrounds the atomic center. In the first place the distending tendency begins to be apparent at about the distance from the atomic center which is defined by the critical volume. It accompanies the atom wherever it goes, under all temperatures and pressures. Existing both in non-electrified substances, and between electrically dissimilar atoms, it is not apparently connected with electric repulsions or with any other manifestation of energy which may be perceived upon a larger scale. Pressure, whether from the chemical attracting of two atoms by one another, or from the cohesive action of molecules upon one another's surfaces, or from impact of collision, or from outside compression, all tend to contract this field of influence at the place or places where the pressure 'is applied. In liquids and solids this distending tendency has been counteracted by affinity and cohesion; and in extreme cases the surface of the atom may, perhaps, be compressed until the atomic diameter is about half of that corresponding to the critical volume. This is, after all, a comparatively small range of compression; evidently the "spring of the atom," whatever it is, increases very rapidly as the atomic centers approach one another. As regards the nature of this distending tendency, it is clearly not directly dependent in any way upon heat vibration. This is shown by the behavior of solids at very low temperatures, at which neither their bulk nor their compressibility are greatly diminished.

These are almost inevitable inferences as regards the outside of the atom, but how the interior may be constituted, other investigations must decide. The present theory makes no necessary postulate as to how the atomic bulk of this so-called "sphere of influence," which I have ventured to call the atom because of its persistence, may be filled. Many sorts of hypotheses will equally satisfy the requirements. There may, indeed, be no such thing as the so-called "substance" in the atom. If, as Larmor and others have suggested, the atom is a minute vacuous space in a prodigiously dense ether, the boundary of the vacuum may be that surface of demarcation capable of being compressed. If, as J. J. Thomson and Rutherford propose, the atom consists of positive and negative corpuscles or electrons held apart by repulsions within themselves and pulled together by an inscrutable attraction, the boundary of this complicated entity (or at least the boundary of the unknown repelling forces which abide in it) must constitute the atom. Such a system would be supposed to be compressible, and all the facts presented in the present discourse seem only what would be expected. According to either point of view or to any other which may be brought forward, it is not necessary to assume that the boundary consists of a perfectly sharp defining surface. Whether the atom consists of "substance," of whirling electrons, of complete vacuity, or merely

of a repellent force, this boundary need not be considered as perfectly sharp. It may gradually diminish with distance without a sharp defining line; but the present research shows that the effect increases inversely as the very high power of the distance; and because we know of no such repelling force on a larger scale (excepting perhaps magnetism, which does not seem to be greatly involved in most cases) it seems not unreasonable to imagine that there is a fairly concrete surface which defines the atom.

The really essential part of the whole discussion lies in the strong evidence that *where affinities are great the atomic centers come closer together, and that where the affinities are slight they are further apart.* This causes each atom to occupy an irregular and distorted space, the shape of which is accountable for many of the properties of matter. The "hard massy particle" of the ancients appears to be a figment of the imagination.

Perhaps to some of you an investigation of this sort may seem very remote from the pressing problems of everyday life. Although we have every reason to believe that we are made of atoms, we do not commonly think of them either in relation to ourselves or to our surroundings. They seem to be an abstract philosophical notion, of little significance in human life; and if atoms themselves are of little significance, why should we bother about their compressibility, or the way in which they fill the space allotted to them? Plausible as this argument may seem, it is really a very short-sighted one. Our dominance over the forces of nature depends primarily upon our understanding of them; and this matter of atomic compressibility, inessential although it may seem, is bound up fundamentally with the very nature of the atoms themselves and the affinities which bind them together. It can afford us new clues as to the intimate working of the Universe and in that way the conception may open up in the future perhaps unexpected and otherwise unattainable insight, and, therefore, unexpected and otherwise unattainable power.

You have doubtless noticed that much of the subject matter of this address has concerned itself with properties and relations which would ordinarily be called physical, although the audience as well as the lecturer are all primarily chemists. There is no anomaly in this. Physics and chemistry are inextricably woven together; they are indeed parts of one science. The organic chemist who would freely use a thermometer for identifying his substance may look with disfavor upon a compression-pump, counting the latter as purely physical implement; but after all the pump is no more physical than the thermometer. The intricacy of the make-up of this world is so great that every means must be sought to help in its untanglement, and we may safely say in these days that the chemist who looks askance upon physics is only half a chemist.

The applications of the theory of compressible atoms to the interpretation of chemical phenomena and to the suggestion of new research are by

no means exhausted by this brief discussion. · No significant objection to it has thus far been encountered; but even supposing that the idea should be supplanted in the future by something yet more satisfactory—and this is always a possibility in the progress of scientific thought—one would be inclined to say that the theory had already justified its existence. The saying of Scripture "By their fruits ye shall know them" applies in full force to theories as well as to persons, and in the short span of its existence the theory has been fruitful. It has "acquired merit" in the only way open to any such hypothesis, namely, by stimulating new experimentation and thus leading to the discovery of facts and laws previously unknown.

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WOLCOTT GIBBS MEMORIAL LABORATORY HARVARD UNIVERSITY,
CAMBRIDGE, MASSACHUSETTS, Sept , 1914

STUDIES OF THE VAPOR PRESSURE OF SOLUTIONS. A STATIC METHOD FOR THE DETERMINATION OF THE DIFFERENCE BETWEEN THE VAPOR PRESSURE OF SOLUTION AND THAT OF SOLVENT.

By J C W FRAZER AND B F LOVELACE
Received October 12, 1914

The fundamental importance of accurate determinations of the effect of dissolved substances on the vapor pressure of solvents, and the lack of agreement of results obtained by different workers using dynamic methods, led the authors, in the spring of 1912, to undertake the problem of improving the static method with the view of making it a method of precision. After some preliminary experiments, they decided to apply the principle of the Rayleigh manometer.[1]

This instrument was designed by Lord Rayleigh for the purpose of measuring small differences in gas pressure. It is used by the authors to measure the difference between the vapor pressure of the solution and that of the pure solvent. The work so far has been limited to aqueous solutions of mannite at 20°.

The essential features of the manometer are shown in Fig 5. R R are glass bulbs, about 39 mm. in diam., blown on a glass fork This is connected by means of a rubber tube with a mercury reservoir which may be adjusted very accurately at any desired height by means of the screw I. At the centers of the bulbs are set two glass points. The side limbs P P communicate with the systems, the relative pressures in which are to be measured.

[1] *Z. physik. Chem.*, 37, 713 (1901); *Trans. Royal Soc.*, 196, 205 (1901).

The bulbs are set in plaster in an iron pot, M, which is mounted on an axis, D, at right angles to the vertical plane passing through the points. This permits of rotation by means of the screw O.

Now, suppose the same pressure exists in the two bulbs. By manipulation of the two screws I and O, the one serving to regulate the height of the mercury and the other to rotate the manometer, the two points can readily be brought into coincidence with their images in the mercury. This is called the zero position.

Now, suppose the pressure in one bulb to be slightly increased. By readjustment of the mercury level and again rotating, the points can a second time be brought into coincidence with their images. It is obvious that, in order to calculate the difference in pressure in the two bulbs, it is necessary to know very accurately the distance between the points and the angle of rotation. The angle of rotation may be calculated from the length of the lever arm, and the rotation and pitch of the screw O. Or, following Rayleigh, we may determine the difference in pressure by means of a mirror, telescope and scale, and this is the method actually used. A is a metallic mirror firmly mounted in a vertical plane perpendicular to the line joining the two glass points. The axis of rotation lies in the plane of the mirror. A telescope, with vertical scale, is mounted at a distance of a little over three meters in front of the mirror, the image of the scale being at all times visible through the telescope.

If d represents the distance between the points, D the distance from mirror to scale, θ the angle of rotation from the zero position, h the difference in pressure in the two limbs of the manometer corresponding to this angle of rotation and S the scale deflection, then the following equations are obtained:

$$h = d \sin \theta \text{ and } S = D \tan 2\theta$$

and

$$h = \frac{ds}{2D} \frac{\sin \theta}{\frac{1}{2} \tan 2\theta}.$$

Now for all values of θ up to $1°$, $\frac{\sin \theta}{\frac{1}{2} \tan 2\theta}$ may be regarded as unity and our formula becomes, $h = ds/2D$. For the particular instrument being used in this work $\theta = 1°$ corresponds approximately to the depression of a 3-molar solution of a nonelectrolyte, $d = 38.88$ mm., and D = 3350.6 mm. Substituting these values and making S = 1 we get, $h = \frac{38.88 \times 1}{2 \times 3350.6} = 0.00580$. This means that 1 mm. scale deflection from zero position corresponds to a difference in pressure in the two bulbs of 0.00580 mm. By observing the points through microscopes of 25 mm. focus, mounted on the instrument and rotating with it, the operator can set the points to an accuracy of 0.1 mm. on the scale,

which corresponds to a difference in pressure of 0.00058 mm. This is the limit of accuracy of the instrument and is approximately that claimed by Rayleigh for his manometer, of which the one used in this work is practically a reproduction.

In using an instrument of such precision the authors are subjecting the static method of measuring vapor pressures to the severest test that could be applied. The results, however, have fully justified its use.

The two great difficulties involved in all static methods for the determination of vapor pressure of solutions, as pointed out by Ostwald and others, are:

1. The necessity for complete removal from the solution of constituents more volatile than the solvent, in particular, dissolved gases, and

2. The necessity of stirring the solution to prevent surface concentration.

In this work, before final observations are made, dissolved air is removd from both solution and solvent to such an extent that, after they have stood in a vacuum for at least forty-eight hours, the pressure due to air in the space above the liquid is negligible. Provision is also made for vigorous stirring always after any appreciable amount of vapor has left the solution. This stirring involves a complete renewal of the entire surface of the solution. The methods by which these two results are accomplished may be best seen by reference to Figs. 1–5, and to the following detailed description of the apparatus and method of manipulation:

The Apparatus.

The entire apparatus is built around the Rayleigh manometer, shown at F, Fig. 1. A more detailed sketch of the manometer is shown in Fig. 5. One side of the manometer communicates with the solvent bulb, H, and the other with the solution bulb I. 1, 2, 3, 4, 5, 6 are mercury traps which serve as stopcocks. They may be opened or closed by adjusting the position of the mercury reservoirs. The long ones are of barometer height, while the short ones are about 100 mm. high. Since ordinary stopcocks are not employed, the use of lubricant is avoided. The large bulb, B, is introduced to increase the capacity of the system and thus facilitate removal of air from solution and solvent. A is a phosphorus pentoxide bulb provided with a ground glass joint and mercury seal. C is the McLeod gage. All connecting tubes are seven mm. internal diameter.

After the apparatus was put together all parts of it except the Rayleigh manometer and the phosphorus pentoxide bulb were thoroughly steamed out.

The bulbs containing solution and solvent are immersed in a water bath, the temperature of which does not vary over periods of several hours more than 0.001°, as read on a Beckmann thermometer. Experience has shown that the Rayleigh manometer is quite sensitive to fluctuations
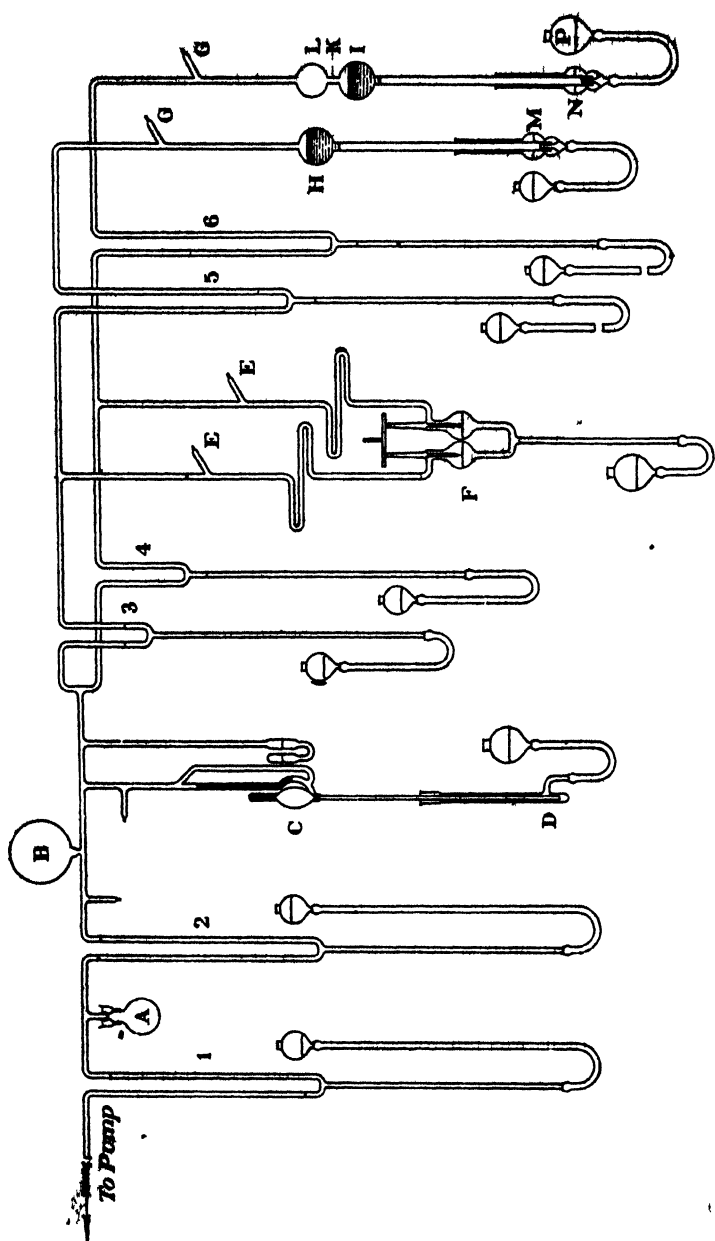
Fig. 1.
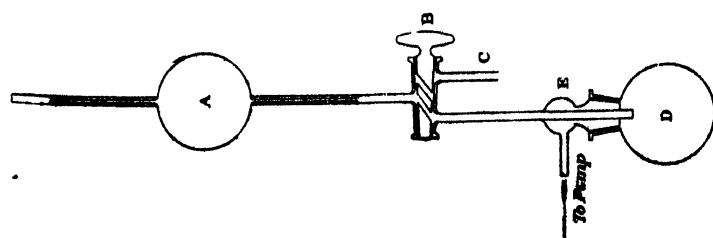
Fig. 5

Fig 4

Fig 3

Fig 2
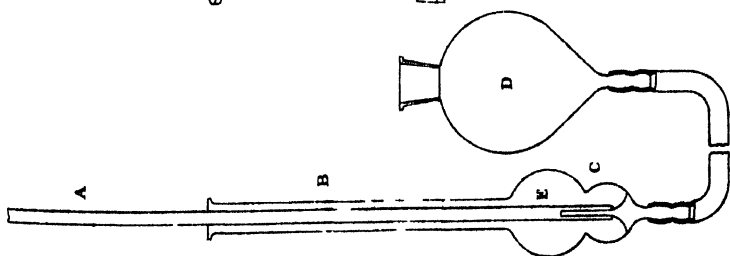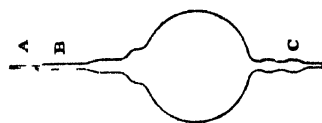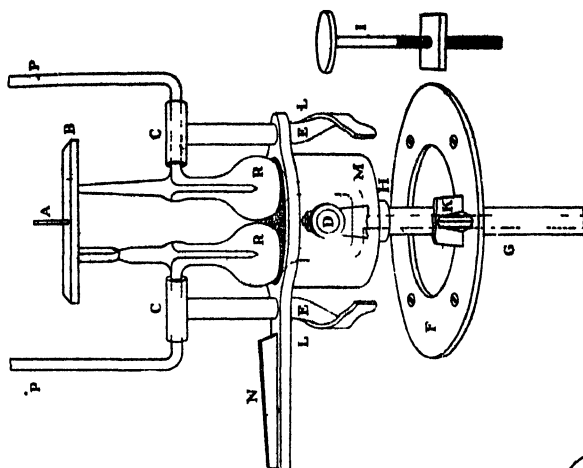
of 0.003° in the bath temperature, if these fluctuations occur over short intervals of time. That is to say, observations of pressure are not constant, if a Beckmann thermometer immersed in the bath shows variations of as much as 0.003°.

While it is thus necessary to avoid sensible variations in the temperature of the solution and solvent, no such constancy of temperature is necessary for the other parts of the system. Large or sudden variations of room temperature are of course to be avoided, but experience has shown that after complete removal of air, slight changes in room temperature do not affect the pressure in the system, and accordingly accurate regulation of room temperature is unnecessary. The temperature of the room is kept several degrees above that of the bath.

In carrying out a complete experiment the following procedure is adopted: The proper amount of carefully cleaned mercury is poured into each of the reservoirs attached to the open ends M and N of the apparatus and the entire system exhausted repeatedly to the highest vacuum attainable by the pump.[1] The zero point is then determined, after which solvent, partially freed from air by boiling, is introduced and the remaining trace of dissolved air removed, as described later. The solution, also partially freed from air, in a manner to be described later, is next introduced and, after complete removal of dissolved air, the zero point may be redetermined. Finally the pressure of vapor over the solution is balanced against that of the vapor over the solvent and the scale deflection read. A detailed description of these processes follows:

The Solvent.—The entire apparatus having been exhausted, trap 5 is closed and the solvent, freed from air as completely as possible by long boiling, is introduced into the bulb from below by means of the arrangement shown in Fig. 3. This is done as follows: A sealed bulb, similar to that shown in Fig. 4 containing air-free solvent, is placed between the mercury reservoir D (Fig. 3) and the trap C and the sealed ends broken off under mercury. Then, regulating pressure by means of the adjustable mercury reservoir, the solvent is forced through the tip and rises through the mercury to the bulb, shown at H in Fig. 1. In this operation the solvent need not come in contact with air and it is, therefore, possible to introduce into the apparatus solvent that is practically air-free. There is, however, in actual practice, always a trace of air to be removed after the solvent is in the bulb. This is accomplished in the following manner: Traps 1, 2 and 4 (Fig. 1) and the McLeod gage are closed, and trap 5 opened and allowed to stay open 24 hours. Trap 5 is then closed and 2 opened. After the absorption of water vapor by the phosphorus pentoxide in A is complete, the McLeod gage is opened and pressure determined.

[1] The pump used is Gaede's rotary mercury pump, with auxiliary oil pump, giving a vacuum of 0.00001 mm.

The residual air is pumped out and the process repeated as many times as may be necessary for complete removal of dissolved air. For practical purposes, the removal of air may be regarded "complete" when, on standing 48 hours in a vacuum, the amount of air given off by the water is so slight that it cannot be detected by means of the McLeod gage; that is, less than 0.0004 mm. The solvent having once been freed from air, may remain in the apparatus indefinitely and it is possible at any time to examine its vapor for air. Trap 3 is now closed and 5 opened.

The Solution.—Fig. 4 shows a device employed for partial removal of air from the solution before it is introduced into the apparatus. The bulb is drawn down at each end to a capillary and enough solution introduced, at the ordinary temperature, to fill the bulb completely at 85–90°. The lower capillary is then sealed off, the upper end drawn down to a very fine capillary, A, (about 0.05 mm.) and the whole heated to the temperature at which the solution completely fills the bulb and capillary. The latter is then sealed off and the solution allowed to cool and stand 24 hours in the partial vacuum thus obtained. The tip of the capillary is next broken off and the process repeated. Five repetitions of this operation are sufficient to remove nearly all the air. The solution is then introduced into the bulb I without coming in contact with the air and the last traces of dissolved air removed in the manner already described for the solvent. The extent to which the solution is concentrated during the process of removal of air after introduction into the bulb I may be accurately calculated and never exceeds 0.1%. After the removal of air is complete, trap 4 is closed and 6 opened, and a measurement may now be taken.

Observations on the Rayleigh manometer during the progress of the removal of air from the solution are very interesting. It is to be remembered that at this stage the vapor pressure of the air-free solvent is balanced against the pressure over the solution, which is equal to the vapor pressure of the solution plus a small air pressure. As long as any air remains in the solution, even the smallest trace, a very long time is necessary for the establishment of equilibrium after the opening of trap 6. The pressure in the solution limb of the manometer, at first very nearly the true vapor pressure of the solution, slowly increases for 24 or 48 hours, depending on how much air remains. After equilibrium is attained, the difference in pressure in the two limbs is read in the usual way by noting the scale deflection. To this apparent depression is added the air pressure in the system, subsequently determined by means of the McLeod gage, after absorption of the water vapor by the phosphorus pentoxide. The depression thus obtained agrees very closely, to about 0.001 mm., with the true depression measured later, after complete removal of air. The following data taken from the laboratory note-book will illustrate this:

Experiment.—150 cc. solution (0.4 M mannite) containing a trace of air were introduced at 11.30 A.M., Jan. 8th.

First Exhaustion.—Trap 4 opened at 12.15 P.M. and solution stirred. Scale Readings, Rayleigh Manometer:

12.30	2.15	5.00	8.00 P.M.	Jan. 9,	9.25 A.M.
51.3	51.0	48.5	46.0		45.0 mm.

Total time, 22 hours, zero 38.0, deflection 7 mm., air pressure 0.054 mm.

Second Exhaustion.—Trap 4 opened at 2.40 P.M., Jan. 9th. Scale Readings:

3.25	3.40	4.15	5.30 P.M.	Jan. 10th, 8.45	10.20 A.M.
57.0	56.6	55.8	54.0	49.5	49.0 mm.

Total time 20 hours. Pressure due to air not read.

Third Exhaustion.—Trap 4 opened at 2.15 P.M., Jan. 10th. Scale Readings.

2.20	2.25	3.00	4.00 P.M.	Jan. 11th, 10.30 A.M.	7.30 P.M.	Jan. 12th, 8.30 A.M.
60.1	59.4	58.0	56.0	53.0	53.0	52.7 mm.

Total time 42 hours.
Deflection 15 mm.

Air pressure......................... 0.036 mm.
Apparent depression.................. 0.087
Correction for air........... .... 0.036

Corrected depression.... .... 0.123

Fourth Exhaustion.—Trap 4 opened at 11.30 A.M., Jan. 12th. Scale readings:

12.00 M.	12.30	2.00	3.00	4.15 P.M.	Jan. 13th, 9.00	10.20 A.M.	2.00 P.M.
59.2	59.2	59.1	58.9	58.7	58.0	57.9	57.9 mm.

Total time 26 hours.
Deflection 20 mm.

Air pressure........................ 0.0068
Apparent depression................. 0.116
Correction for air.................. 0 007

Depression........................ 0.123

Fifth Exhaustion.—Trap 4 opened at 5.00 P.M., Jan. 13th. Scale readings:

5.15	7.45 P.M.	Jan. 14th, 9.45 A.M.	12.40	3.15 P.M.
61.0	59.7	59.1	59.5	59.3 mm.

Time 23 hours.

Air pressure................... 0.000
Depression................... 0.124 mm.

The true depression, as later determined, was 0.122 mm.

The gradual development of pressure in the solution side of the manometer, as seen in the first four exhaustions, was due to the slow escape of dissolved air. The air pressure developed, however, became less with each exhaustion; still, even in the fourth exhaustion, when the equilibrium pressure of air was very small, a very long time was necessary for complete equilibrium to be established. When the solution becomes air-free, equilibrium is always reached in from 15-20 minutes.

It should be pointed out that the foregoing figures, obtained during the time air is being removed from the solution, are not regarded as final. No attempt is made to regulate the bath temperature with any great accuracy while air is being removed, the variations sometimes amounting

to 0.005° during this operation, and no special effort was expended to make the above measurements anything more than approximately correct. Final measurements are always made after no more air can be pumped off from the solution and while these final measurements are being made the bath temperature never varies more than 0.001° over periods of several hours.

When the apparatus was being built the McLeod gage was included in the system for the purpose of showing when the removal of air was complete. As a matter of fact, however, the gauge is not necessary for this purpose. Given an air-free solvent in one bulb, the operator can follow very closely the progress of removal of air from the solution in the other bulb by observations on the Rayleigh manometer and can tell infallibly, without use of the McLeod gage, when the removal of air is complete.

Stirring the Solution.—Efficient stirring of the solution is desirable because it facilitates the removal of air; it is necessary, when readings are to be made, in order to destroy the surface concentration of the solution resulting from evaporation. The device shown in Fig. 3, which permits the introduction of the solution as has already been described, also serves as a means of stirring. The stirring is brought about by simply raising and lowering the mercury in the reservoir P, Fig. 1. About one-half of the solution is in this way forced through the constriction K into the upper bulb L, and back again. Several repetitions of this procedure insure practically complete uniformity of concentration throughout the whole solution.

The apparatus shown in Fig. 2 was devised for the purpose of preparing the solution in a vacuum.

Experimental.

We give below the results of two experiments with aqueous solutions of mannite. The solutions are made up on the weight-normal basis; that is, by a molar solution is meant one containing a gram molecular weight of solute in one thousand grams of solvent. In making up the solutions, allowance is made for the known amount of solvent that is to be lost during subsequent removal of dissolved air, and the concentrations given are the concentrations at the time final observations are made.

Experiment 3.—0.5 M mannite.

The solution was introduced into the apparatus on the afternoon of November 12, 1913. On November 20, the air was completely removed. This solution was under examination throughout the month of December and in January the following final observations were made.

It will be observed that each of the above experiments lasted about eight weeks. The object of continuing observations over such long periods was, once for all, to make a thorough investigation of all sources of error

Experiment 3, using 0.5 *M* mannite.
Solution introduced Nov. 12, 1913.   Removal of air complete Nov. 20th.   Final observations as follows:

Date	Item	Readings	Mean	Deflection
Jan. 1	Zero at varying intervals	37.9 37.9 37.9	37.97	} 26.86
Jan. 2		37.8 38.0 37.9 38.0 38.1 38.2 38.0 38.0	64.83	
Jan. 3	Reading (5 min. intervals)	64.8 64.8 64.9	64.93	} 26.93
Jan. 3	Reading (5 min. intervals)	64.9 65.0 64.9	38.00	
Jan. 5	Zero (5 min. intervals)	38.0 38.0 38.0	64.93	} 26.93
	Reading	64.9 64.9 65.0	38.00	
	Zero	38.0 38.0 38.0		

Mean Deflection 26.91.   Depression 26.91 × 0.00580 = 0.156 mm.   Temp. 20.036°.

Experiment 4, using 0.4 *M* mannite.
Solution introduced Jan. 8, 1914.   Removal of air complete Jan. 16th.   Final observations as follows:

Date	Item	Readings	Mean	Deflection
Jan. 22	Reading (at various intervals)	58.9 58.9 58.9 58.9 58.9 58.9 58.8 58.8 58.9	58.9	20.9
	Zero	38.0 38.0 38.0	38.0	
Jan. 24	Zero	37.9 37.9 38.0	37.93	
	Reading	58.9 59.0 59.1	59.0	21.07
Jan. 27	Reading	58.8 58.8 59.0	58.87	
	Zero	38.0 38.0 38.0	38.00	20.87
Jan. 28	Zero	38.0 38.0 38.0	38.0	
	Reading	59.0 58.9 59.0 59.0 59.0 58.9	59.0	21.0
Feb. 5	Reading	58.8 59.0 58.8 58.8	58.85	
	Zero	37.8 37.9 37.8	37.83	21.02
Feb. 6	Reading	59.0 58.9 59.0 59.0 59.0	59.0	
	Zero	38.0 38.0 38.0	38.0	21.0
Feb. 14	Reading	59.0 59.0 59.0	59.0	
	Zero	37.9 38.0 37.9	37.93	21.07
Feb. 28	Reading	58.0 58.0 58.0 58.0	58.0	
	Zero	37.0 37.0 37.0	37.0	21.0
March 2	Reading	58.2 58.0 58.0 58.0	58.05	
	Zero	37.0 37.0 37.0	37.0	21.05
March 3	Reading	58.0 58.1 58.1	58.06	
	Zero	37.0 37.0 37.0	37.0	21.06

Mean of all observations (Jan. 28–Mar. 3) Deflection 21.03; Depression 21.03 × 0.0058 = 0.122 mm.   Temp. 20.008°.

and to determine the limits of accuracy of the method. These experiments have shown conclusively that:

1. Variations of temperature of solution and solvent must not exceed 0.002°.

2. Accurate regulation of the temperature of other parts of the apparatus, i. e., those parts containing vapor, is unnecessary. This is because, when all air has been eliminated, equilibrium between solution and vapor is very quickly established, so that slight changes of temperature, unless they are too sudden, merely cause evaporation or condensation of slight amounts of water, without affecting pressure. If the system contains air, a change of temperature will produce change in pressure and such fluctuations are quite noticeable even with a very small amount of air.

3. If the temperature of the bath is controlled to within 0.001°, readings of pressure are constant to within 0.001 mm.

The authors believe that the measurements recorded above differ from the true values by not more than 0.001 mm. and are convinced that, with certain minor changes, the method is capable of giving results which are accurate to the third decimal place.

The experiments recorded above were made in collaboration with Mr. E. Miller who is continuing the work, and the authors expect to investigate solutions of both electrolytes and nonelectrolytes in various solvents.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

VAPOR PRESSURES OF CERTAIN ALCOHOLIC SOLUTIONS.

BY O. F. TOWER AND A. F. O. GERMANN.

In a former paper one of us described a method for measuring vapor pressures by means of the Morley gage.[1]   Satisfactory results were obtained with aqueous solutions, but with non-aqueous solutions certain difficulties were encountered which rendered the results that were reported at that time of little value.   Moreover, the opinion was expressed that possibly the air-bubbling method would yield better results with this latter class of solutions.   Numerous trials since then have, however, convinced us that it has no advantages over the method with the Morley gage, except at temperatures above room-temperature, and, besides, it possesses some disadvantages of its own which have caused us to return to the method with the Morley gage.   The present paper, therefore, describes certain improvements in the apparatus and method of treatment of the solutions in determining the vapor pressures of non-aqueous solutions by this method.

The gage and the method of carrying out the readings were described

[1] O. F. Tower, THIS JOURNAL, 30, 1219 (1908).

in detail in the former paper and need not be repeated here. The accompanying photograph will give an idea of the general appearance of the new apparatus. The gage GG is in the background, while the tubes containing the solvent and the solutions MM' are shown in the foreground.
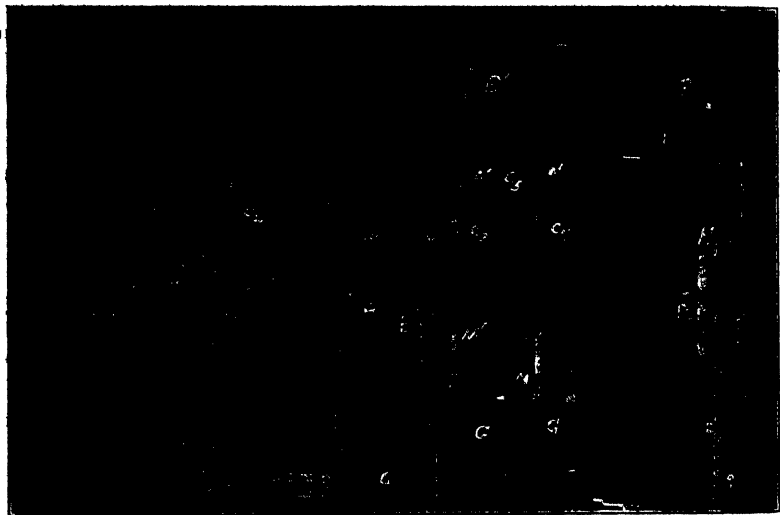
The principal improvement in the apparatus is the arrangenemt for purifying the solvent and introducing it into the tubes M and M' entirely out of contact with air. This portion of the apparatus was modeled after that used in Ph. A. Guye's laboratory (Geneva) for the purification of gases by liquefaction and fractional distillation in a vacuum. The removable flask A, in which the preliminary purification and desiccation were carried out, was connected by means of a carefully ground-in glass joint to the reflux condenser B, filled with glass beads. This communicated with the fractional distillation tubes D_1 and D_2 through stopcocks C_1 and C_2. Each tube was provided with a mercury manometer and vacuum connections to both water suction and mercury pumps. The former was connected at W through fused calcium chloride; the latter, of the type described by Cardoso and one of us,[1] at P through phosphorus pentoxide. All stopcocks were lubricated with viscous rubber grease, soluble in ether but not in alcohol.

After the solvent had been purified, as well as possible, in contact with the air, the containing flask A was placed in position and the air and any dissolved gases pumped out with the water suction pump. Then the bulk of the liquid was distilled at room-temperature into D_1, rejecting the

[1] Germann and Cardoso, *J. chim. phys.*, 10, 306 (1912).

higher boiling fractions. Just previously D_1 had been rinsed out with the vapor of the liquid to be introduced,[1] and during the distillation it was surrounded by a mixture of ice and salt.   Then followed a series of fractional distillations between D_1 and D_2, always discarding the first and last fractions as the least pure.

The next step was to secure a sample of the purified solvent from which weighed portions could be introduced into the vapor pressure tubes, out of contact with the air.   This was accomplished by means of the weighing tubes EE, each provided with a stopcock and a flat ground joint ee.[2] These weighing tubes were secured to the apparatus by means of brass screw clamps.[3]   The solvent was distilled into one of these tubes.   One of the two following methods was then used to introduce the liquid into the vapor tension tubes: M was first filled to a suitable height with the pure solvent, after having been completely evacuated, dried in contact with phosphorus pentoxide, and rinsed several times with the vapor of the solvent.   By the first method the filling was accomplished by simple distillation from the weighing tube.   From a theoretical standpoint this method of procedure must result in giving two fractions in M and M', with a very small difference of vapor tension, without the pr sence of the dissolved salt in M'.   This would therefore influence, to a slight extent, the magnitude of $p - p'$.   Practically the error thus caused would be vanishingly small, owing to the care taken in purifying the solvent.   However, to be on the safe side this method was abondoned, and the following method was employed in our later work:

M and M' were provided with special exit tubes, extending vertically upward, bearing the stopcocks C_3 and C_4, and terminating in flat ground joints.   This enabled fixing the weighing tube containing the solvent in an inverted position over the vapor tension tubes, as shown at E'.   The capillary tubes between C_3, or C_4, and the stopcock of the weighing tube were provided with vacuum connections, so that they could be evacuated independently of other portions of the apparatus.[4]   Then by opening the two stopcocks concerned, the solvent flowed through the capillary connecting tubes into M or M'; the stopcock of the weighing tube was closed when the nesessary volume of solvent had flowed out, M was cooled with cold water or ice for a few minutes, and finally the weighing tube was removed.[5]

[1] In a general way the precautions exercised throughout the preliminary operations were the same as those described in detail by Germann (*J chim phys.*, **12**, 66 (1914)).

[2] The advantage of these joints over those ordinarily used is that any two make a pair, so that they are interchangeable.   For detailed drawing and description, see Guye, *Arch. Sci. phys. nat*, Geneva, [4] **27**, 586 (1909).

[3] For drawings and details see Boubnoff and Guye, *J. chim. phys*, **9**, 295 (1911).

[4] This was also true of every portion of the apparatus capable of isolation.

[5] It may be objected that in both methods the weight of solvent introduced into

A simplified Macleod pressure gage, H, was used to evaluate the degree of vacuum in the apparatus. The phosphorus pentoxide tube R was used to evacuate the apparatus when alcohol vapors alone were present, this by virtue of its affinity for the alcohols.

The readings were made at a temperature of 15°, instead of at 0° as in the former series, for the reason that the vapor pressures being higher at this temperature, $p - p'$ would have a greater magnitude, and could thus be read off with less relative error. The temperature was maintained by surrounding the tubes MM' with a water-bath, through which water at 15° was constantly circulating.

The solvents employed were methyl and ethyl alcohol. It was therefore necessary to determine their vapor pressures at 15°, which was done in exactly the same manner as described in the former paper for determining these pressures at 0°;[1] i. e., by means of a manometer connecting with the tube M. Behind the manometer was a millimeter scale, on which the mercury heights were read off by means of a cathetometer. These readings were made at frequent intervals during the course of the year and varied but little. The average values of a large number of such observations are:

<div align="center">

Vapor pressure at 15°.

Methyl alcohol...................... 73.61[2] mm.

Ethyl alcohol.... .... 32.18[3] mm.

</div>

Potassium iodide, lithium chloride and benzil[4] were the substances used as solutes. Each of these represented to a certain extent a different type. Potassium iodide is an electrolyte which has little tendency to combine with solvents; lithium chloride is an electrolyte which is very hygroscopic, i. e., it has a tendency to combine with the solvent; benzil

M', found by taking the difference between the weights of the weighing tube before and after filling M', would be too great by the amount of vapor remaining in the tubes between the weighing tube and M', when the stopcocks were closed. However, the volume of these tubes was made as small as possible by using very short lengths and by selecting tubes of small bore—capillary tubes in the second method. In the first method the pressure was quite small—a few millimeters only—since the distillation was carried out at about —20°; in the second method the pressure was somewhat higher, but the volume was very much smaller, so that the amount of solvent lost under the most exaggerated conditions was always less than the accuracy of the weighings. Assuming, for example, in the first method, one meter of glass tubing 5 mm. in diam., filled with vapor at 20° over the liquid solvent at —10°, the loss would be 0.05 mg. with methyl alcohol, and 0.03 mg. with ethyl alcohol.

[1] Tower, Loc. cit., p. 1228.

[2] 34 measurements; probable error of average 0.016 mm.

[3] 15 measurements; probable error of average 0.028 mm.

[4] We also attempted to use tetramethylammonium iodide, but found it so slightly soluble in the alcohols that no very trustworthy results could be obtained. Two of our best determinations with this substance dissolved in methyl alcohol are given in the table and are also shown in the curves for the sake of comparison.

is a nonelectrolyte and a nonhygroscopic substance. These were all purified preparations of C. A. F. Kahlbaum. The first was further purified by repeated crystallization from methyl alcohol. The lithium chloride was precipitated from aqueous solution by saturation with hydrogen chloride gas. The benzil was not further purified.

No fundamental changes were made in the gage portion of the apparatus, and therefore the readings were made precisely as described in the former paper.[1] It may however, be noted that M and M' were made of soft glass instead of Jena glass, and that the mercury valve between M and M' was replaced by a stopcock, C_6, as was also the valve between the vapor pressures tube and the mercury pump. A new lot of specially well-ground Geissler stopcocks were employed throughout the apparatus and gave excellent satisfaction. We were, therefore, not troubled by leaks about the stopcocks, which was sometimes the case in the former work. While making a reading, M and M' were constantly shaken, as otherwise there was a great variation in the values obtained. Even under the best conditions and with the great care exercised, considerable fluctuations in the reading would sometimes occur which were entirely inexplainable. This was especially true when using dilute solutions. In such cases readings were repeated under different conditions until a set which remained fairly constant was obtained. All of this consumed a great deal of time. Besides, with a complicated apparatus of this kind, leaks would frequently occur which were difficult to locate, so that the progress of the work was very slow. This can easily be understood when it is stated that the gathering of the results given in this paper occupied our available time for about twelve months.

The results are given in the accompanying tables. The headings of the first two columns are easily intelligible. The third column gives the lowering of the vapor pressure produced by the dissolved substance as obtained from the gage readings ($p =$ the vapor pressure of the pure solvent, $p' =$ the vapor pressure of the solution). The fourth column contains the molecular weight of the solute, calculated from the formula, $m = \dfrac{gM}{p - p'/p'}$.[2] The fifth column, n, gives mols of solute dissolved in one mol of solvent. The sixth column contains an expression, the value of which ought to be constant, if there is no change of molecular state.

The results have also been plotted in curves, using the observed lowering of the vapor pressure as ordinates and the concentrations of Column 2 as abscissas. The most probable trend of the curve in each case is seen to be a straight line. This is to be expected from a consideration of the

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[1] Tower, *Loc. cit.*, p. 1223.

[2] *Loc. cit*, Formula 1, p. 1224. Formula 2 might have been employed, but the values differ very little from those obtained from Formula 1.

SOLVENT, METHYL ALCOHOL, (VAPOR TENSION AT 15°, 73.61 MM.).

Solute, Potassium Iodide (M. W., 166.02).

Gram solute in 1 g. solvent.	Grams solute in 1 mol solvent.	$p - p'$.	m.	n.	$\dfrac{p-p'}{n}$.
0.13673	4.379	3.230	95.4	0.02636	119.7
0.12686	4.063	2.918	98.4	0.02444	119.4
0.10664	3.416	2.484	97.8	0.02057	120.8
0.09469	3.033	2.1855	99.1	0.01825	119.8
0.09167	2.936	2.1265	98.7	0.01767	120.6
0.077245	2.474	1.780	99.8	0.01489	119.5
0.06566	2.103	1.514	100.2	0.01267	119.5
0.05744	1.840	1.324	100 4	0.01107	119.6
0.04883	1.564	1.123	100.9	0.00942	119.2
0.04350	1.393	0 974	103.8	0.00839	116.1
0.03266	1.046	0.798	95.5	0.00630	126.7
0.01726	0.5528	0.423	95.7	0.00333	127.0
0.009803	0.3044	0.238	93.9	0.00183	130.1
0.006181	0.1980	0.154	94.5	0.00119	129.4
0.003709	0.1188	0.0743	117.6	0.000716	103.8
0.002192	0.0702	0.0577	89.4	0.000423	108.4

Solute, Lithium Chloride (M. W., 42.40).

0.05434	1.741	5.76	20.5	0 04103	140.4
0.04170	1.336	4.34	21.3	0.03150	137.8
0.03352	1.074	3.344	22.6	0.02533	132.0
0.03073	0.9843	2.868	24.3	0.02320	123.6
0.02689	0.8612	2.660	23.0	0.02032	130.9
0.02144	0.6869	2.057	23.9	0.01620	127.0
0.01718	0.5504	1.740	22.7	0.01298	134.1
0.01682	0.5388	1.542	25.2	0.01270	121.4
0.01195	0.3828	1.125	24.7	0.00903	124.6
0.009587	0.3071	1.0065	22.1	0.00724	139.0
0.009218	0.2953	0.7768	27.7	0.00697	111.5
0.007165	0.2295	0.7627	21.9	0.00541	141.0
0.006195	0.1984	0.5871	24.7	0.00468	125.4
0.005123	0.1641	0.3923	30.6	0.00387	101.4
0.002451	0.0785	0.1448	39.8	0.00185	78.3

Solute, Tetramethylammonium Iodide (M. W., 201.03).

0.003865	0.1238	0.0397	229 3	0.000616	64.4
0.002890	0.09256	0.0218	312.4	0 000461	47.3

Solute, Benzil (M. W., 210.08).

0.03662	1.173	0.332	259.0	0.00558	59.5
0.03144	1.007	0.320	230.7	0.00479	66.8
0.020665	0.6619	0.192	253.2	0.00315	60.9
0.01055	0.3380	0.100	248.4	0.00161	62.1

SOLVENT, ETHYL ALCOHOL (VAPOR TENSION AT 15°, 32.18 MM.).

Solute, Potassium Iodide (M. W., 166.02).

0.01671	0.7694	0.1897	129.7	0.00463	41.0
0.009916	0.4566	0.1127	129.8	0.00275	41.0
0.006134	0.2825	0.0628	144.0	0.00170	36.9

SOLVENT, ETHYL ALCOHOL (VAPOR TENSION AT 15°, 32.18 MM.) (*Continued*).

Gram solute in 1 g solvent	Grams solute in 1 mol solvent	$p — p'$	m	n.	$\dfrac{p — p'}{n}$.
		Solute, Lithium Chloride (M W , 42 40)			
0 03824	1 761	1 795	29 8	0 04156	43 2
0 03685	1 697	1 770	29 1	0 04002	44 2
0 02088	0 9614	1 1585	25 8	0 02268	51 1
0 01726	0 7947	0 7538	33 1	0 01875	40 2
0 01186	0 5463	0 4870	35 6	0 01289	37 8
0 009425	0 4340	0 3397	40 7	0 01024	33 2
		Solute, Benzil (M W , 210 08)			
0 02823	1 300	0 198	210	0 00619	32 0
0 01543	0 7105	0 119	191	0 00338	35 2
0 007968	0 3669	0 0590	200	0 00175	33 7
0 004260	0 1962	0 0295	214	0 000934	31 6

calculated molecular weights of Column 4 In the case of potassium iodide and lithium chloride these quantities are less than the formula weights, as might be predicted. The strange thing is that the values are so constant throughout the different dilutions. In other words, the calcu-

$p-p'$ in millimeters of Mercury

$p-p'$ in mm of Mercury

o *LiCl* in C_2H_5OH
‣ *KI* in C_2H_5OH
x$(C_4H_5CO)_2$ in C_2H_5OH

Grams Solute in 1 Mol Solvent

o *LiCl* in CH_3OH
□ *KI* in CH_3OH
! $(C_4H_5CO)_2$ in CH_3OH
x$(CH_3)_4 NI$ in CH_3OH

Grams Solute in 1 Mol· Solvent
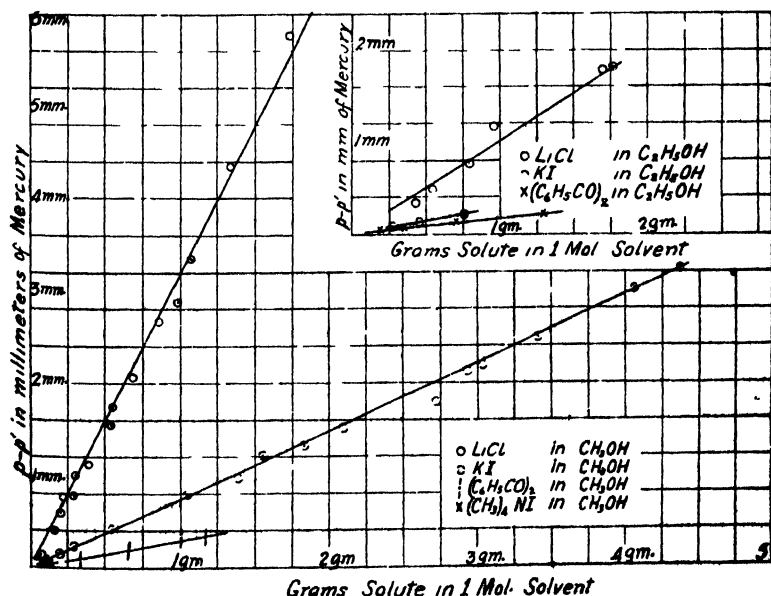
lated molecular weights do not show that these salts are any more dissociated in dilute solution than in concentrated. This is also confirmed by the ebullioscopic measurements of Jones[1] with potassium iodide in

[1] *Z. physik. Chem* , **31**, 129, *et seq.* (1899).

methyl and ethyl alcohols. He found the degree of dissociation to be very nearly constant in both cases, and to have a value of about 50% in methyl alcohol and 25% in ethyl alcohol. This is exactly in accord with our values for the lowering of the vapor tension. The conductivity determinations of Zelinsky and Krapiwin[1] showed substantially the same thing, although other observers[2] have found that the molecular conductivity increases with the dilution in very dilute solutions.

Why the calculated molecular weight should remain constant over such a range of concentrations is difficult to explain. It may have something to do with the combination of the salts with the solvents and to the progressive combination of the ions with the solvents. However, in such a case, one would not expect potassium iodide to be so subject to these effects as lithium chloride.[3] If, in plotting the curves, the values of n, in the fifth column, had been used as abscissas instead of the concentrations of the second column, all of the curves would be thrown closer together, and those of potassium iodide and lithium chloride in methyl alcohol would be almost superimposed, indicating almost identical molecular states.

As to benzil, its molecular weight in ethyl alcohol seems to be normal, while in methyl alcohol it seems to be associated with one or two molecules of the solvent.

MORLEY CHEMICAL LABORATORY,
WESTERN RESERVE UNIVERSITY,
CLEVELAND, OHIO

A MODIFIED PRECISION BAROMETER.

BY ALBERT F. O. GERMANN.

In the determination of the densities of gases by the various precision methods involving the measurement of volume, pressure, temperature, and mass,[4] the evaluation of the pressure is perhaps the most difficult, and the values obtained for this factor are always much less accurate than those obtained for the temperature, volume, and mass, particularly when the first two are taken at the temperature of melting ice, and the mass is taken as the average of the mass of several samples of gas simultaneously taken. A gr at many special barometers and manometers have been designed in a effort to eliminate the errors to which this type

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[1] Z. physik. Chem., 21, 3, (1896).

[2] See Carrara, Gass. chim ital, [1] 26, 119 (1896); also Turner, Am. Chem. J., 40, 558 (1908).

[3] According to Turner and Bissett, J. Chem. Soc., 103, 1904 (1913), lithium chloride forms no compounds with methyl alcohol above 10°, but with ethyl alcohol LiCl.-4C₂H₅OH exists up to a temperature of 17.4°.

[4] See, for example, article by the author, J. chim. phys., 12, 66 (1914).

of instrument is subject, chief of which are the residual pressure in the barometric vacuum, and variations in the meniscus. Both objections would appear to be remedied in the barometer of wide bore, the vacuum chamber of which communicates with a mercury pump; here capillarity no longer exercises an appreciable influence; the meniscus, therefore, is perfectly flat, except at the edge; and the quality of the vacuum is under the experimenter's direct observations and control. But even here concordant readings cannot be abtained, because of various disturbing factors, such as non-uniformity of temperature, even when surrounded by an air bath, and the difficulty of getting a sharp reading of the position of a large mercury surface. Experience with this type of barometer has nevertheless demonstrated its superiority over the type composed of narrow tubing, where meniscus corrections must be made, and over the type sealed at the top, which may be expected to give low readings, unless filled while boiling the mercury and simultaneously making a vacuum with a good mercury pump. Barometers filled in this way, however, may not be successful, because a meniscus often fails to form in those portions of the barometer tube which have been heated to drive out air, due to, some change in the glass. At the École de Chimie in Geneva, the author remembers seeing one barometer of this type stand for a week, without a suggestion of a meniscus; then one morning a perfect meniscus appeared, only to disappear after a day or two, never to appear again.

It would seem, then, that to secure the most uniform results, it would be imperative not to subject those portions of the barometer tube in which the mercury surfaces are to rest, to a high temperature. The barometer must, then, not be permanently sealed, so as to permit of the removal of the traces of air adhering to the glass, which are slowly given up under the decreased pressure. One device for doing this is to terminate the barometer with some form of stopcock[1] through which the accumulated air may be expelled; or the vacuum chamber may communicate with a mercury pump. The first method is open to the objection raised by Professor Morley against all stopcocks used in connection with a vacuum— a stopcock is usually nothing more than a located leak; the other method is expensive and more or less time-consuming, since each stroke of the pump removes only a definite fraction of the residual air in the barometer. This objection suggested to the author the combination of pump and barometer into one instrument; similar modifications have been described, but because of certain practical objections, have not been adopted in research laboratories. The type described below has met with approval in several European laboratories, and may be found useful in this country. A knowledge of the simpler operations of glassblowing is, of course, necessary for its construction

[1] R. A. Baker, This Journal, 35, 199 (1913).

The barometer (see figure) is really a modification of the mercury pump described by Cardoso and the author,[1] in which the main reservoir has been omitted. The two branches, L_1 and L_2, are, as usual, cut from the same glass tube, and connected at the bottom by means of the narrow U-tube U. The short branch L_2, about 20 cm. long, has sealed into it at P a colored glass point, to which the lower mercury surface may be ad-

justed in making a reading; the gaseous pressure to be measured is admitted through the stopcock C_3. The U-tube has sealed into it at D a T-tube bearing the stopcocks C_1 and C_2, each of which is lubricated with Acheson graphite, rather than with stopcock grease, to keep the mercury clean; since the graphite has no adhesive power, the stoppers are held in place by means of brass stopcock clamps, any air admitted with the mercury collects at E, and may be expelled through C_2. The other branch, L_1, which measures about 110 cm., terminates in a fine capillary tube B, about 76 cm. long and 0.2 mm. bore, bent down so as to rest against the barometer tube L_1; the lower end of B is bent upwards and bears a wide tube R, which may be connected to the water pump via the stopcock C_4 and the drying tubes containing P_2O_5 and fused $CaCl_2$.
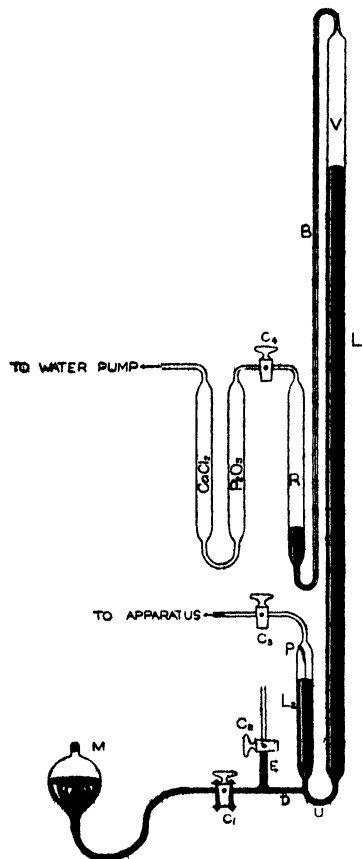
After careful cleansing with appropriate reagents, and rinsing with distilled water, the barometer should be dried by passing a slow current of dry air through it for a week; this insures the removal of traces of moisture in the pores of the glass. Then the instrument may be mounted on a suitable support, against a graduated glass plate, and filled. To carry out this operation, stopcocks C_2 and C_3 are closed, and C_1 and C_4 opened. Freshly distilled mercury is poured into the reservoir M, which is connected to the barometer by means of a rubber tube, and gentle suction applied through the drying tubes and C_4 by means of the water pump; or

[1] Germann and Cardoso, *J. chim. phys.*, **10**, 306 (1912).

the water pump may be dispensed with at this point if the rubber tube be long enough to allow M to be raised to the top of the barometer. Mercury is allowed to completely fill the tube L_1, and to run over into the reservoir R, into which the air has been driven. Then the bulb M is lowered, the mercury in L_1 subsides to a point at which it is in equilibrium with the air enclosed in L_2; the level of the mercury in L_2 may be adjusted to the glass point by opening the stopcock C_1 and adjusting the height of the mercury bulb M; the air admitted with the mercury, and which has collected at E, may be expelled through C_2. If the length of the capillary B has been properly adjusted, any great excess of mercury in R will be forced back into V by the pressure of the atmosphere; B must, however, not be shorter than the maximum local barometric height to prevent the totality of the mercury from being forced back with the resultant destruction of the vacuum.

After several days, a certain amount of air will have disengaged itself from the glass walls of V, and the barometer will consequently give too low a reading. This may be verified by lifting the bulb M until the mercury rises in V, and approaches the mercury thread in the capillary; the minute volume of air present prevents the mercury surfaces from meeting. The test is an extremely delicate one, because the air in question is under a very small pressure; and if an effort be made to expel it, it may adhere to the capillary walls of B, when the volume has been sufficiently reduced by the increasing pressure. To effect the expulsion of the air,[1] it then becomes necessary to make a partial vacuum in R, by turning on the water pump; the air bubble expands, and is forced out. A single operation of this kind always suffices to test the vacuum, and to get rid of the merest traces of gas.

While working on the densities of oxygen and air,[2] the author had an opportunity of comparing two barometers of the type described with two others whose vacua were controlled by means of a mercury pump; one of the latter served as standard, as its internal diameter was about 25 mm., and hence no meniscus corrections had to be made; the others had a diameter of approximately 15 mm. Corrections for capillarity were very small, but were nevertheless made, applying the following considerations, suggested by Ph. A. Guye.

[1] As a matter of fact, it may be readily shown that this small amount of gas may be left in the barometer without, in any appreciable way, affecting the barometric reading. Assuming the volume of V to be 35 cc., the diam. of the capillary 0.2 mm., and the length of the thread of air in the capillary 5 mm., under a pressure of, say, 5 cm. of mercury, a simple calculation will show that the pressure of this volume of air amounted, in the 35 cc., to approximately 0.00001 mm.

[2] *Compt. rend.*, **157**, 926 (1913); *J. chim. phys*, **12**, 66 (1914); Germann, "Geneva Thesis," No. 514.

Laplace[1] has shown that

$$p = A \left(\frac{1}{R} + \frac{1}{R'} \right)$$

where A is the capillary constant and p the pressure in mm. of water due to the capillary action in various directions of a liquid surface, whose principal radii of curvature are R and R'. For practical purposes, we may consider that R and R' are equal; then

$$p = \frac{2A}{R}.$$

Laplace found by experiment for mercury $A = 44.07$; Desains found $A = 45.97$; using the mean of these values, we have for p, expressed in mm. of mercury:

$$p = \frac{2 \times 45}{13.56} \frac{1}{R} = \frac{C}{R}$$

where C is a constant equal to 6.6.

Besides this, the following corrections were applied:
(a) for the thermal expansion of mercury
(b) for the thermal expansion of the glass scale
(c) for altitude and latitude, i. e., for gravity

Combining (a) and (b) into a single correction, which we will denote by τ, and denoting the correction for gravity by G_0 we have the expression for the corrected barometric height:

$$H = G_0(h + p_s - p_i - \tau)$$

where h is the uncorrected distance between the lower edge of the two menisci; p_s the pressure exercised by the upper meniscus, and p_i that exercised by the lower meniscus; but

$$p_s - p_i = c \left(\frac{1}{R_s} - \frac{1}{R_i} \right)$$

whence

$$H = G_0 \left[h + c \left(\frac{1}{R_s} - \frac{1}{R_i} \right) - \tau \right]$$

The value of $1/R$ varies with the height, f, of the meniscus and becomes approximately equal to zero with a flat meniscus, when it becomes superfluous to read the lower edge; this was the case with the 25 mm. barometer.

To facilitate the calculation of $c(1/R_s - 1/R_i)$, a curve was prepared for each barometer plotting as ordinates the possible meniscus heights, and the corresponding values of $1/R$ as abscissas· knowing the height, f, of the meniscus, the value of $1/R$ may be read directly from the curve. To construct the curves, the following method may be employed: A number of concentric arcs are constructed on millimeter paper; in each a

[1] *Annuaire du Bureau des Longitudes*, Paris, 1912, p. 533.

chord is drawn equal in length to the internal diameter of the barometer for which the curve is to serve; the length of the mid-ordinate[1] of the arc subtended by the chord gives the value of f, and from the radius R of the arc the corresponding value of $1/R$ may be calculated.

The value of τ, correction for the thermal expansion of mercury and glass scale, may be taken from any table of physical constants.

The gravity correction G_0 is here taken, not as an additive correction, as is customary, but as a fractional one, for the sake of simplicity. Its value is the ratio of the normal acceleration due to gravity g_n (at sea level and $45°$ N. latitude) to the acceleration due to gravity at the place of measurement, g_m. For Geneva this ratio becomes[2]

$$G_o = \frac{g_n}{g_m} = \frac{980.616}{980.599} = 1\ 000017$$

which is a positive correction of approximately 2 in 100,000, a negligible quantity.

Table I contains the data obtained in two sets of readings with these barometers, being the values obtained in the course of two series of determinations of the density of air in Geneva No. 1 is the standard 25 mm. barometer, II is one similar to it, having a diameter of 13 5 mm III and IV are of the type described above, each of 15 mm. internal diameter. The values of h given are the averages of several readings, $t°$ is the average of the temperatures shown by four carefully checked thermometers, placed at various points along the mercury column.

TABLE I

Series	No	h	$t°$	r	f_s	f_i	$c\left(\dfrac{1}{R_s} - \dfrac{1}{R_i}\right)$	H
VII .	I	764 9	16 5	2 18				762 72
VII	II	764 95	16 35	2 16	1 25	1 30	—0 01	762 78
VII	III	764 8	16 45	2 17	1 00	0 90	+0 02	762 65
VII	IV	764 9	16 4	2 17	1 00	1 00		762 73
VIII .	I	762 8	15 6	2 06 .				760 74
VIII	II	762.7	15 5	2 04	1 30	1 25	+0 01	760 67
VIII .	III	762 7	15 5	2 04	1 10	1 00	+0 02	760 68
VIII. . . .	IV	762 85	15 6	2 06	1 05	1 00	+0 01	760 80

This plainly demonstrates the dependability of the pressure readings obtained with barometers III and IV. At the same time it shows the impossibility of getting as concordant results as, for example, in the determination of volumes, where it is possible for different experimenters to check each other to within one part in thirty or forty thousand, without any very great precautions. Obviously, too, a much higher degree of

[1] In the sense in which the term is used in surveying, viz., the outer segment of a radius cut by a perpendicular chord

[2] *Recueil de Constantes Physiques*, 1913, pp 93 and 96.

accuracy in the determinations of gaseous pressures may be obtained by the simultaneous use, as above, of several good barometers.

THE MORLEY CHEMICAL LABORATORY,
WESTERN RESERVE UNIVERSITY,
CLEVELAND, OHIO.

A QUALITATIVE TEST FOR WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION.[1]

By E. R. WEAVER.

CONTENTS.

Outline of method and previous related work. (a) Preparation of Reagents. Anhydrous Solvents; Cuprous Salt Solutions; Removal of Acetylene from Calcium Carbide. (b) Methods of Making Test: Blank Tests. (c) Compounds Interfering with Test: Action of Acids; Tests of Oleic Acid and Glycerol. (d) Sensitiveness of Test. (e) Summary.

In the course of the examination of certain carefully purified organic compounds[2] it was found that a simple, quick and very delicate qualitative test for water, showing approximately the amount present, can be made in the following manner: The substance under examination is placed in contact with calcium carbide in the presence of a solvent for acetylene, and any acetylene formed by the action of water is detected by adding the resultant solution to an ammoniacal solution of cuprous chloride. The following paper describes the application of this method simply as a qualitative test for water. A large amount of work has already been done with a view to applying the acetylene-cuprous chloride reaction to the quantitative determination of both water and acetylene, and a colorimetric method for acetylene depending upon the formation of copper carbide in a colloidal form has been devised. The publication of this work is planned for the near future.

Calcium carbide has recently been quite extensively used for the determination of water in substances which, for any reason, do not permit the application of the more usual methods of analysis. It was suggested by Berthelot,[3] that the acetylene evolved in the reaction could be determined by absorption in an ammoniacal solution of a silver salt with subsequent titration of the excess of silver. This method was tried by Rivett[4] for the determination of water in butter, but was not successful on account of the incomplete absorption of the evolved acetylene. With this exception, all the chemists who have used the calcium carbide method seem to have determined the evolved acetylene either volumetrically or by loss in weight. Obviously, neither of these methods is applicable to

[1] Published by permission of the Director of the Bureau of Standards.

[2] THIS JOURNAL, 35, 1309 (1913).

[3] Compt. rend., 129, 361 (1899).

[4] Chem. News, 104, 261 (1911).

the detection of very small amounts of water, especially in the presence of other volatile substances.

Preparation of Reagents.

Preparation of Anhydrous Solvents.—When testing for water in organic liquids it is usually most convenient to allow the liquid under test to serve as the solvent for acetylene, in which case the previous preparation of an anhydrous solvent is not necessary. In applying the tests to solids, however, it is necessary to allow the reaction with carbide to take place in the presence of an anhydrous liquid, preferably a solvent of the substance under test; and the first difficulty met with in the use of the method was that of preparing even approximately dry solvents. Samples of gasoline, benzene, ether, ethyl acetate, amyl alcohol, amyl acetate, ethyl alcohol, methyl alcohol, acetone, chloroform, carbon tetrachloride, carbon disulfide, and pyridine were treated with calcium chloride, lime, metallic sodium, metallic calcium, and phosphorus pentoxide, except in those cases·where a given drying agent was known to be inapplicable on account of reaction with the solvent. The five solvents first mentioned were thus prepared so nearly free from water that it was impossible to detect a trace of acetylene dissolved in them after several minutes' contact with calcium carbide. Sodium appeared to be the best drying agent for the hydrocarbons and ether, and calcium for the esters. Drying of the other solvents was not carried to completion by the above treatment, but all except pyridine were dried sufficiently to be used successfully as solvents for substances containing any considerable amount of water. The list could, no doubt, be extended almost indefinitely, and nearly all, if not all, of those mentioned, could be completely dried by the use of proper drying agents and the observance of suitable precautions. All the liquids tested in this investigation were found to dissolve enough acetylene to give the desired test. Since any of these solvents will, if exposed to the air for a very short time, absorb enough water to show a decisive test, they should be kept, after being dried, in bottles containing some of the drying agent and communicating with the air through a tube containing phosphorus pentoxide; since it is difficult to exclude the air sufficiently by the use of ordinary glass cork, or rubber stoppers unless the pressure differences, due to temperature changes, are eliminated by the use of a drying tube.

The most sensitive tests are obtained when a solvent is employed which is immiscible with water, since the precipitate formed by the subsequent treatment with cuprous chloride solution, if small in amount collects at the surface of separation of the two liquids and is very easily detected. If a fairly large amount of acetylene is present the aqueous layer dissolves enough acetylene to form a precipitate throughout the solution. When the acetylene is dissolved in liquids miscible with water,

such as alcohol and acetone, the copper carbide first appears in a colloidal form, giving an intense red color to the liquid, but a visible precipitate quickly separates out. Since the precipitate is distributed through a much larger volume when these solvents are used, the test is not nearly so sensitive as with ether or chloroform with which, as above noted, the precipitate is concentrated in a single layer. Furthermore, with some of the miscible solvents, especially with acetone, the precipitation does not appear to be always complete. In fact, it is sometimes possible to discharge the color of a colloidal solution of copper carbide by adding a large excess of acetone.

Preparation of Cuprous Chloride Solution.—The test for acetylene is most conveniently made by the use of an ammoniacal solution of a copper salt reduced by hydroxylamine. Such solutions were used by Ilosvay[1] for the detection of acetylene in gas, and the methods of preparation which would give the most sensitive reagent were carefully investigated. He recommends the following proportions for solutions made from several salts:

1. 0.75 g. copper chloride ($CuCl_2.3H_2O$), 1.5 g. ammonium chloride, 3 cc. ammonium hydroxide (20–21% NH_3), 3 g. hydroxylamine hydrochloride.

2. 1 g. copper nitrate ($Cu(NO_3)_2.5H_2O$), 4 cc. ammonium hydroxide, 3 g. hydroxylamine hydrochloride.

3. 1 g. copper sulfate ($CuSO_4.5H_2O$), 4 cc. ammonium hydroxide, 3 g. hydroxylamine hydrochloride.

In each case the copper salt is dissolved in a small amount of water, the ammonia and hydroxylamine hydrochloride are added and the solution is diluted to 50 cc. The first of these solutions seems, in general, to give the most satisfactory results. This solution may be used for the detection of acetylene in any of the solvents previously mentioned except carbon bisulfide, which is reduced to hydrogen sulfide by hydroxylamine and precipitates the copper from the solution as a sulfide. When it is necessary to use carbon bisulfide as a solvent the precipitating solution must be made up from cuprous chloride without the use of any reducing agent. It is very difficult to prepare such a solution which is entirely colorless, but a very small precipitate of copper carbide may be readily detected even in a deep blue solution, and tests have shown that the presence of a cupric salt does not interfere with precipitation, provided a sufficient amount of the cuprous salt is present.

On account of the difficulty caused by the oxidation of cuprous to cupric chloride, experiments were made with a view to replacing the copper solution with an ammoniacal solution of a silver salt; but the white or yellowish precipitate of silver carbide was so much less characteristic

[1] *Ber.*, **32**, 697 (1899).

and so much harder to detect in small amounts than the red copper carbide, that the formation of the latter is the more useful test even when, as in the presence of carbon bisulfide, the copper solution used cannot be decolorized.

Removal of Acetylene from Calcium Carbide.—Commercial calcium carbide always contains a considerable amount of occluded acetylene, formed by interaction with moist air, which must be removed before any delicate test can be made for water in solution. It is very difficult to remove this acetylene completely even by ignition in an evacuated tube, but it may be completely driven off by boiling the carbide with one or two portions of the anhydrous solvent, the liquid being completely evaporated before the carbide is used. In case it is not desired to use, for this purpose, the solvent which is subsequently employed in the water determination, anhydrous ether may always be used.

Method of Making Test.—The test for water is carried out most simply by adding the substance to be tested, together with the solvent, to a few pieces of calcium carbide which have been "boiled out," as described in the preceding paragraph, in a test tube. The test tube is closed by a dry cork or other stopper and shaken occasionally without allowing the liquid to touch the stopper. Two or three minutes' contact with the carbide is usually sufficient. The tube is allowed to stand long enough for the carbide to settle and the clear solvent decanted into the cuprous solution, with which it is vigorously shaken. It might be supposed that small particles of carbide would be carried into the aqueous solution and that the acetylene so produced would make the test of no value; but very little difficulty is experienced from this source. The high density of the carbide causes even very small piece to settle rapidly, and particles which are carried into the precipitating solution are immediately surrounded by a dense precipitate which causes them to appear as black specks easily distinguished from the bright red, flocculent precipitate produced by dissolved acetylene.

In case a more rigid examination for water is desired, the method may be very easily modified to permit suitable precautions to be taken to exclude moisture from the air· and the probability of error from particles of calcium carbide carried mechanically into the aqueous solution may be avoided by distilling the solvent, together with the dissolved acetylene, into the precipitating solution. In case the latter method is adopted, it is most convenient to distil in a stream of hydrogen dried over phosphorus pentoxide.

In testing solids, it is preferable to use as a solvent for the acetylene a liquid which also dissolves the solid under examination. This is not absolutely necessary however, since an anhydrous liquid will generally extract water quite readily from a solid containing it, provided the solid

is in a fine state of division. Tests for water in powdered sugar have been made successfully by the use of ether, in which sugar is nearly, if not entirely, insoluble. Tests of nonvolatile acids or other compounds, which it is not desirable to bring into contact with carbide, may be made by adding an anhydrous liquid, which is then distilled off and tested for water, either by passing over carbide in vapor form or in the usual manner after condensation. Gases may be tested by simply passing over carbide, which has been freed from acetylene, and into the cuprous chloride solution.

Blank Tests.—Whatever procedure is adopted, it is necessary to make a blank test before using the method to detect water in the sample under examination. When testing an organic liquid by simple contact with carbide and decantation, it is only necessary to insure the removal of all acetylene previously held by the carbide. Boiling out two or three times with the liquid under test or with ether, in the manner already dsecribed, is always sufficient to accomplish this. Any acetylene found in portions of the liquid subsequently added is due to water in the sample. When using an anhydrous solvent or when distilling in hydrogen it is necessary to make the blank test in the same manner as the test for water.

Compounds Interfering with the Test.—The usefulness of any qualitative test is, of course, largely determined by the number of compounds which will give the reaction in question. Masson[1] states that of all the substances dealt with in ordinary circumstances, water is the only one which has any chemical action on carbide. A consideration of the reaction between water and calcium carbide and that occurring in neutralization shows that in the presence of an acid, water might be expected to form as rapidly as it is removed until the hydrogen of the acid has been quantitatively converted into acetylene by the following cycle of reactions:

$$CaC_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + C_2H_2$$
$$Ca(OH)_2 + 2H(A) = Ca(A)_2 + 2H_2O$$
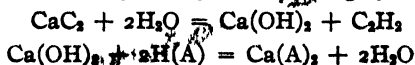
In the case of the weaker organic acids, at least, this does not take place, probably because of the fact that no neutralization occurs in a nearly anhydrous solution, and the formation of acetylene seems to give a good qualitative test for water in spite of the possible reaction between the acid and calcium hydroxide.

Masson found that crystalline acids and acid salts, including those which contain water of crystallization readily removed by calcium carbide, do not react as acids, when treated with calcium carbide, with either the carbide or the calcium hydroxide resulting from reaction with the water of crystallization. Experiments by the author with acids in anhydrous solution showed that in some cases, at least, the acid in solution

[1] *Chem. News*, **103**, 37-8 (1911); *J. Chem. Soc.*, **97**, 851 (1910).

is quite as inactive as were the acids in Masson's experiments. Thus a 1 g. sample of fused benzoic acid was dissolved in ether and boiled with calcium carbide under a reflux condenser for fifteen minutes without producing a trace of acetylene. Solutions of oleic and phthalic acids have been found to behave in the same manner. Ordinary glacial acetic acid reacts vigorously with the production of acetylene; but neither acetic anhydride, nor acetic acid containing a considerable excess of acetic anhydride do so. Sulfuric acid of all concentrations, including that containing an excess of sulfur trioxide, causes a continuous slow evolution of acetylene. Even in cases when acetylene is evolved on testing the weaker organic acids, it would, of course, be impossible to say, without first testing acids of known water content, how much, if any, of the acetylene was formed by the acid itself.

In his experiments upon the determination of water by the measurement of the acetylene evolved, McNeil[1] found that a larger volume of gas was evolved from glycerol and from oleic acid than could be accounted for by the amount of water present. In view of the behavior of related compounds, it seemed improbable that this could be due to the production of acetylene from the compounds themselves, except that in the case of oleic acid continuous neutralization and reaction with the water so formed might be expected to take place as with any other acid. In order to test this point, thoroughly dried samples of the two compounds were prepared. The large water content of the best samples available was not materially reduced by heating for three hours at 100°, in a stream of air dried over phosphorus pentoxide and at a pressure of less than half an atmosphere. The oleic acid was therefore dissolved in anhydrous ether, the ether distilled off under reduced pressure and the acid heated to 110°. This operation was repeated several times. Glycerol was treated in the same way, using alcohol as a solvent instead of ether. By this procedure, both oleic acid and glycerol were obtained which did not give any trace of acetylene after contact with calcium carbide, either when used alone or in solution in ether or alcohol. An elevated temperature (as high as 120°) did not cause any reaction which could be detected.

Sensitiveness of Test.—This method for the detection of water is very sensitive. Numerous tests were made by the simple method of decantation of the solvent after contact with carbide, using samples of gasoline, benzene, and ether, which gave perfect blank tests. Known amounts of water were introduced by adding nearly absolute alcohol, the water content of which had been determined by Mr. E. C. McKelvy of this Bureau by the method of critical solution temperature.[2]

The results indicated about the same degree of sensibility in the case

[1] *Bureau of Chemistry, Circular No. 97 (1912).*

[2] *Bull. Bur. Standards, 9, 344.*

of the three above-named solvents, 0.01–0.03 mg. of water per cc. of the solution in contact with the carbide being the limit at which the formation of a precipitate could be detected. Other tests made by adding a known weight of water dissolved in anhydrous ether showed about the same sensibility. Tests made upon other solvents, in which a blank test showed a trace of water, indicated that the test made with alcohol was less sensitive than with the solvents mentioned above, but more sensitive than with acetone. Ethyl acetate, chloroform and carbon tetrachloride showed about the same sensibility as ether.

Summary.

A qualitative test for water, sensitive to less than 0.1 mg. may be very easily and quickly made by bringing the substance to be tested into contact with calcium carbide in the presence of a solvent for acetylene, which is then decanted or distilled into an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for use, if carefully dried. The method is applicable to a great variety of substances and especially to volatile organic compounds. The only compounds known to interfere with the test are the stronger acids and substances, such as hydrogen sulfide, which precipitate cuprous salts from solution.

WASHINGTON, D C.

THE FREE ENERGY OF THE VARIOUS FORMS OF ELEMENTARY SULFUR.

BY GILBERT N. LEWIS AND MERLE RANDALL

No other element is known to occur in as many different forms as sulfur. Several solid modifications have been studied, of which we shall, for the present, consider only the familiar rhombic and monoclinic forms, S_R and S_M. Rhombic sulfur, being the stable form at room temperature, will be taken as the standard and will therefore be assumed to possess zero free energy and zero heat content. In the liquid state two distinct substances are present, known as S_λ and S_μ (soluble and insoluble sulfur).[1] In the gaseous state at least four modifications have been studied: S, S_2, S_6 and S_8.

Monoclinic Sulfur.

$S_R = S_M$.—The heat capacity of rhombic sulfur has been determined by numerous investigators.[2] When all their data are plotted the most

[1] Since this paper was written a third kind of sulfur in the liquid state, S_π, has been described by Aten (Z physik. Chem., 86, 1 (1913)). His results do not necessitate any material change in the present calculations, nor do they suffice to warrant us at present in attempting to calculate the standard free energies of the several liquid forms.

[2] Regnault, Ann. chim. phys., [3] 9, 322 (1843); Kopp, Trans. Roy. Soc. London, 155, I, 71 (1865); Bunsen, Ann. physik., [2] 141, 1 (1870); Dewar, Proc. Roy. Soc.

probable values for the heat capacity at various temperatures fall on a somewhat curved line, which, however, may be regarded as straight between $0°$ and $100°$, and expressed by the equation

$$C_p(S_R) = 4.12 + 0.0047T \text{ cal. per gram atom.} \tag{1}$$

Similarly, the available data[1] for monoclinic sulfur lead to the following equation as the most probable linear expression for the heat capacity between $0°$ and $100°$.

$$C_p(S_M) = 3.62 + 0.0072T \tag{2}$$

Hence for the reaction considered

$$\Delta\Gamma = \Delta C_p = -0.50 + 0.0025T. \tag{3}$$

The best value for the heat of transition is probably that of Brönsted,[2]

$$\Delta H_{273} = 77.0, \quad \cdot$$

hence by combination with the preceding expression we find[3]

$$\Delta H = 120 - 0.50T + 0.00125T^2. \tag{4}$$

We may now write the equation for the increase of free energy[4]

$$\Delta F° = \Delta H_0 - \Delta\Gamma_0 T \ln T - \frac{1}{2}\Delta\Gamma_1 T^2 + IT;$$

or

$$S_M = S_R; \quad \Delta F° = 120 + 0.50 T \ln T - 0.00125T^2 - 2.820T. \tag{5}$$

The value of I being determined as follows: The temperature at which the free energy change of this reaction is zero, in other words, the transition point, is given by Tammann[5] as $94.6°$ and by Reicher[6] as $95.5°$. We will take the mean, $95°$. We may, therefore, substitute in the preceding equation and find $I = -2.820$, whence $\Delta F°_{298} = 17.5$. $\quad \cdot$

The free energy change at $25°$ was also found directly by Brönsted[7] who determined the relative solubility of the two forms of sulfur in benzene, in ethyl ether, in ethyl bromide, and in ethyl alcohol. The ratio of the concentration of S_M to that of S_R was found to be 1.27, 1.28, 1.28, and 1.3 in the four solvents, respectively. Since both forms of sulfur were shown by Brönsted to give identical solutions with the formula S_8, the free energy change is given by the equation $\qquad$

London, **76**, 332 (1905); Forch and Nordmeyer, *Ann. physik.*, **20**, 423 (1906); Wigand, *Z. physik Chem.*, **63**, 293 (1908); Nernst, Koref and Lindemann, *Sitzb. Kgl. preuss. Akad. Wiss.*, **12, 13**, 247–261 (1910); Nernst, *Ibid.*, **12, 13**, 261–282 (1910).

[1] Regnault, *Loc. cit.*; Thoulet and Lagarde, *Compt. rend.*, **94**, 1512 (1882); Wigand, *Loc. cit.*; Nernst, Koref and Lindemann, and Nernst, *Ibid.*

[2] Brönsted, *Z. physik. Chem*, **55**, 371 (1906)

[3] This equation gives at $95°$ $\Delta H = 105$, while Tammann, *Ann. physik.*, [3] **68**, 633 (1899) obtained the value 100 at this temperature. See also Lewis and Randall, THIS JOURNAL, **33**, 488 (1911).

[4] Lewis, THIS JOURNAL, **35**, 1 (1913), Equation 32.

[5] Tammann, *Loc. cit.*

[6] Reicher, *Z. Krystallographie*, **8**, 593 (1884).

[7] Brönsted, *Loc. cit.*

$$\Delta F^\circ = \frac{R'T}{8} \ln 1.28.$$

Hence $\Delta F^\circ_{298} = 18.3$, a value nearly the same as that found by the other method, 17.5, which value will be used hereafter.

Liquid Sulfur.

While it is probable that a large number of pure liquids contain two or more molecular species in equilibrium with one another, the case of sulfur is peculiar in that the equilibrium under certain circumstances is established so slowly that it has been possible to demonstrate the existence in the liquid state of the two substances known as S_λ and S_μ, and to determine quantitatively at various temperatures the relative amounts of these two substances (which in all probability have the formulae S_8 and S_6, respectively).[1] We have, therefore, three reactions to consider, involving the formation from the standard rhombic sulfur of pure S_λ, of pure S_μ and of the mixture of the two as they exist together in equilibrium, which may be denoted by $S_{\lambda,\mu}$. Of these only the first and last have been fully investigated.

$S_R = S_\lambda$.—The heat capacity of S_λ is given by the equation[2]

$$C_p(S_\lambda) = 5.4 + 0.005T. \tag{6}$$

Combining this with (1) we have for the reaction,

$$\Delta\Gamma = 1.28 + 0.0003T \tag{7}$$

and

$$\Delta H = \Delta H_0 + 1.28T + 0.00015T^2. \tag{8}$$

ΔH_{273} is[3] 467 and thus $\Delta H_0 = -35$ and

$$\Delta F^\circ = -35 - 1.28T\ln T - 0.00015T^2 + 7.77T. \tag{9}$$

The value of $I = 7.77$ in this equation was obtained as follows: Kruyt[4] found that when rhombic sulfur melts to form pure S_λ the melting point[5] is 112.8°. At this temperature, therefore, $\Delta F^\circ = 0$, and the above equation may be solved for I. From this equation we find $\Delta F^\circ_{298} = 94$ cal.

$S_M = S_\lambda$.—We may make a similar calculation for this reaction. The melting point[6] of S_M to form pure S_λ is 119°. This, together with the heat capacities and heats of transition already used, leads to the equation

$$\Delta F^\circ = -155 - 1.78T\ln T + 0.0011T^2 + 10.60T. \tag{10}$$

Subtracting this equation from (9) gives an equation identical with (5) except that $I = -2.83$ instead of $I = -2.82$.

[1] Our evidence on the basis of which we attribute the formula S_6 to S_μ, is given in a letter published by Smith and Carson, Z. physik. Chem., 77, 672 (1911).

[2] Lewis and Randall, THIS JOURNAL, 33, 476 (1911).

[3] Lewis and Randall, Ibid.

[4] Kruyt, Z. physik. Chem., 64, 513 (1908), where a bibliography of earlier work on the different forms of sulfur may be found.

[5] See also Smith and Carson, Z. physik. Chem., 77, 668 (1911).

[6] Smith and Holmes (Z. physik. Chem., 42, 469 (1903)) give 119.25°; Wigand in a later paper gives 118.95° (Z. physik. Chem., 75, 235 (1910)).

This is not the only way of checking the accuracy of the various numerical data employed. Given the equation for $S_R = S_\lambda$, and the melting points of S_R and S_M, we could have calculated without further data ΔH for $S_M = S_\lambda$, and for $S_R = S_M$, and would have obtained values in close agreement with those which we have used. Or we could have assumed the experimental values of ΔH, and then from either of the melting points the other one could have been calculated, just as the transition point, $S_R = S_M$, can be calculated from (9) and (10) when the two melting points are known.

Besides the melting points when S_R and S_M melt to form pure S_λ, we have also the so-called natural melting points, namely, the temperatures at which the solids are respectively, in equilibrium with $S_{\lambda,\mu}$, the stable mixture of S_λ and S_μ. The natural melting point of S_R is 110.4° (Kruyt,[1] 110.6°; Smith and Carson,[2] 110.2°). The natural melting point of S_M[1] is 114.6°. From either of these experimental points we may calculate the free energy of the equilibrium liquid, or with the known data for the heat content of the various forms we may, from the first of these points, calculate the second point, and this calculation gives a value within 0.2° of the one experimentally determined.

$S_\lambda = S_{\lambda,\mu}$.—There is still another way of calculating the free energy of the equilibrium liquid, $S_{\lambda,\mu}$. With decreasing temperature the equilibrium liquid becomes more and more nearly pure S_λ. It would therefore be a very close approximation to the truth to assume that at 25° the free energy of $S_{\lambda,\mu}$ is equal to that of S_λ; or, better, since by extrapolation from data about to be mentioned we find the amount of S_λ converted into S_μ at 25° to be about 0.8%, we may assume that in this very dilute solution the activity of the S_λ is proportional to its mol. fraction, and thus we find by a very simple calculation that $\Delta F°_{298} = $ —0.8 cal.

Next from the thermal data it is possible to calculate the free energy of $S_{\lambda,\mu}$ at higher temperatures. In this case, however, the use of the thermal data cannot be made conveniently in the ordinary way, for, as we have shown in the paper dealing with the heat content of sulfur, the specific heat of the equilibrium liquid cannot be expressed as any simple algebraic function of the temperature. We must therefore go back to the fundamental free energy equation which we may write in the form

$$d\left(\frac{\Delta F}{T}\right) = -\frac{\Delta H}{T^2}\, dT$$

or, when integrated between two temperatures, T_1 and T_2,

$$\frac{\Delta F_2}{T_2} - \frac{\Delta F_1}{T_1} = \int_{T_1}^{T_2} -\frac{\Delta H}{T^2}\, dT.$$

[1] Kruyt, Loc. cit.
[2] Smith and Carson, Z. physik. Chem., 77, 661 (1911).

Now, if $\Delta H/T^2$ is plotted against T, we may perform the indicated integration graphically and thus obtain the free energy at one temperature when it is known at some other temperature. This is the general method which must be employed when the heat of reaction is known at various temperatures, but cannot be conveniently expressed in terms of a simple equation.

The value of ΔH in the formation of 32 g. of S_μ from S_λ we have shown to be 416 cal. The specific heat of S_μ is unknown, but we shall make no serious error in assuming that it is approximately the same as that of S_λ, and therefore ΔH for $S_\lambda = S_\mu$ is approximately constant, and ΔH for $S_\lambda = S_{\lambda,\mu}$ is simply $416x$ where x is the fraction of S_μ in $S_{\lambda,\mu}$. Substituting this value for ΔH in the above equation, we have only to integrate $-416x/T^2 dT$. Now from the data of Smith and Holmes[1] and of Carson[2] (see Fig. 1, Lewis and Randall)[3] we have plotted the values of x/T^2 between 25° and 445° and determined graphically the area of this curve between 25° and various upper temperature limits, thus obtaining the following table, in which the first column gives the absolute temperature, the second the fraction of S_μ, the third the value of the integral, and the fourth the value of $\Delta F°$ at each temperature provided that $\Delta F°_{298} = 0$:

TABLE I.

T.	x.	$\int_{298}^{T} -\frac{416x}{T^2} dt.$	$\Delta F°$.
298	0.008	0.0	0.0
373	0.031	—0.00465	— 1.7
393	0.040	—0.00664	— 2.6
413	0.055	—0.00902	— 3.7
423	0.067	—0.01037	— 4.4
433	0.111	—0.01217	— 5 3
443	0.187	—0.01553	— 6 9
453	0.225	—0.01981	— 9.0
473	0.270	—0.0295	—14.0
510	0.313	—0.0496	—25.3
573	0.332	—0 0771	—44.2
653	0.338	—0.1070	—70.0
718	0.341	—0.1267	—91.0

The value of $\Delta F°$ for $S_\lambda = S_{\lambda,\mu}$ at 110.4° can be very readily found from independent data already given, for, this being the natural melting point of S_R, $\Delta F° = 0$ for $S_R = S_{\lambda,\mu}$ and therefore $\Delta F°$ for $S_\lambda = S_{\lambda,\mu}$ is equal to $-\Delta F°$ for $S_R = S_\lambda$. The latter value may be obtained from Equation 9, or, since the interval from this temperature to the point of equilibrium between S_R and S_λ is small, we shall obtain greater accuracy by simplifying the primitive equation

[1] Smith and Holmes, Z. physik. Chem., 54, 257 (1905).

[2] Carson, THIS JOURNAL, 29, 499 (1909).

[3] Lewis and Randall, Ibid., 33, 476 (1911).

$$\Delta F - \Delta H = T \frac{d(\Delta F)}{dT}$$

to

$$-\Delta H = T \frac{d\Delta F}{dT} .$$

and regarding the small temperature interval as an infinitesimal. We thus find at $110.4°$ for $S_R = S_\lambda$, $\Delta F° = 2.7$, and thus for $S_\lambda = S_{\lambda,\mu}$ $\Delta F° = -2.7$ cal. The value obtained by interpolation in Table I is -2.2 if $\Delta F°_{298} = 0$, or -3.0 if $\Delta F°_{298} = -0.8$, as it was roughly estimated. These calculations have been entered into in more detail than would be warranted by the importance of the particular problem involved, but they afford simple illustrations of the methods which are generally applicable in similar cases.

Gaseous Sulfur.

The next reactions to be considered involve not only much larger free energy changes, but also greater uncertainty in these values The gaseous phase of sulfur is even more complex than the liquid, and may contain at least four molecular species—S, S_2, S_6 and S_8. We shall attempt to determine the free energy of only one of these, namely, S_2, although the measurements of Nernst[1] on the dissociation $S_2 = 2S$, and those of Preuner and Schupp[2] on the equilibrium between S_2, S_6 and S_8 make it possible to estimate roughly the free energy of the other gaseous forms.

$2S_{\lambda,\mu} = S_2$.—In order to find at the temperature of boiling $S_{\lambda,\mu}$ the difference in free energy between the equilibrium vapor and S_2 at atmospheric pressure (if it could so exist) we will make use of the following device: Let us assume that the equilibrium vapor is expanded reversibly and isothermally to such a low pressure that it is essentially pure S_2, and that then, with the aid, perhaps, of a negative catalyzer, the S_2 vapor is compressed reversibly and isothermally to atmospheric pressure without the formation of any S_6 or S_8. The difference between the values of $\int v dp$ in the two isotherms will be the desired difference in free energy. Now the isotherm of S_2 may be assumed to be that of a perfect gas, that of the equilibrium vapor can be obtained from measurements of the volume of sulfur vapor at different pressures. When we first made this calculation the best available data were those of Biltz and Preuner[3] who determined the density of sulfur vapor at $444.6°$ between 14 mm. and 458 mm. The relations which they thus obtained between pressure and volume were plotted and the curve extended, as accurately as the data permitted, to one atmosphere on the one side and to 0.0075 atmos-

[1] Nernst, Z. Elektrochem., 9, 622 (1903).

[2] Preuner and Schupp, Z. physik. Chem., 68, 129 (1909).

[3] Biltz and Preuner, Ibid., 39, 322 (1902).

phere on the other, and the area corresponding to the integral, $\int vdp$, was determined graphically and found to be 97.0 liter atmospheres. Now, assuming that at the lower limit of pressure the sulfur vapor is all S_2, the other isotherm is an equilateral hyperbola coinciding with the first curve at the lower pressures. The corresponding area under this curve was 289 liter atmospheres. The difference of 192 liter atmospheres, or 4650 cal., should be the difference in free energy of the gas S_2 and the liquid $S_{\lambda,\mu}$ at one atmosphere and 444.6°, since the liquid $S_{\lambda,\mu}$ has the same free energy as the equilibrium vapor.

The data from which this calculation was made were subject to considerable uncertainties, which, however, were in part removed by the publication of a more extended investigation on the isotherm of sulfur vapor by Preuner and Schupp.[1] Their results permitted an independent application of the method just outlined. Since these measurements were made at 450°, in order to reduce their results to the boiling point of sulfur a small correction had to be made, details of which need not, however, be given. The final result thus obtained was 4300 cal. We will take as a mean of the two determinations

$$2S_{\lambda,\mu}(l) = S_2(g); \ \Delta F°_{718} = 4500 \text{ cal.}$$

$2S_R = S_2$.—We then have from Equation 9

$$S_R = S_\lambda; \ \Delta F°_{718} = -590 \text{ cal.}$$

From Table I

$$S_\lambda = S_{\lambda,\mu}; \ \Delta F°_{718} = -90 \text{ cal.}$$

By combining the three data we find

$$2S_R = S_2 \ (g., 1 \text{ atmos.}); \ \Delta F°_{718} = 3140 \text{ cal.}$$

In order to find the expression for this free energy change at other temperatures, we must know the heat of the reaction as a function of the temperature. The heat capacity of S_R has been given in Equation 1, that of the gas S_2 will be assumed to be the same as that of oxygen, namely,[2]

$$C_p(S_2) = 6.5 + 0.0010T. \quad (11)$$

Hence

$$\Delta\Gamma = 1.74 - 0.0084T. \quad (12)$$

The value of ΔH_o we may obtain by combining the heat of formation of H_2S from S_2 found by Preuner and Schupp[3] at 1000° with the heat of formation of H_2S from S_R found by Thomsen and Berthelot at room temperature. This calculation, of which the details will be given in the paper on hydrogen sulfide, yields the value $\Delta H_o = 29600$. We may now make use of the value which we have obtained for $\Delta F°_{718}$ and write as the final equation

[1] Preuner and Schupp, Z. physik. Chem., 68, 129 (1909).
[2] Lewis and Randall, This Journal, 34, 1130 (1912).
[3] Preuner and Schupp, Z. physik. Chem., 68, 157 (1909).

$$2S_R = S_2 \, (g); \; \Delta F^\circ = 29600 + 1.74 T \ln T + 0.0042 T^2 - 51.3 T, \quad (13)$$
and
$$\Delta F^\circ_{298} = 17600.$$

We wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the forms of sulfur considered in this paper:

TABLE II.

Substance.	F°_{298}.	Equation.	Substance.	F°_{298}.	Equation.
S_R...........	0	..	$S_{\lambda,\mu}$........	—0 8	(Table I)
S_M...........	17.5	5	S_2	17600	13
S_λ	94	9			

BERKELEY, CAL.

DETERMINATION OF CUPROUS AND CUPRIC SULFIDE IN MIXTURES OF ONE ANOTHER.

BY EUGEN POSNJAK.

In the course of an investigation upon copper sulfide minerals, which at the present time is being carried out in this laboratory, it became necessary to discover a method to determine cuprous and cupric sulfide in their mixtures. Such a determination involves great difficulties for the reason that no solvents are known for either of them, i. e., solvents which dissolve them without decomposition. It was therefore necessary to find a substance that would react with only one of the components, or, if reacting with both of them, would yield with each of them a different substance, which in turn could in some way be easily separated and determined.

Several reactions were tried, for instance the oxidation of cuprous sulfide. It is well known that cuprous sulfide changes in an acid solution in the presence of oxygen into cupric sulfide. But experiments showed that this reaction did not stop at cupric sulfide, and that cupric sulfide was also much attacked under these conditions. Finally it was found that the reaction of cuprous and cupric sulfide with silver nitrate offered, under certain conditions, a method for their determination.

The reaction between cuprous sulfide and silver salts has been examined by Heumann,[1] Schneider[2] and more recently by C. Palmer and E. S. Bastin.[3] As a result, this reaction has been expressed by the equation

$$Cu_2S + 2Ag_2SO_4 = Ag_2S + 2Ag + 2CuSO_4$$

[1] Ber., 7, 1680 (1874).
[2] Pogg. Ann. Physik., 152, 471 (1874).
[3] Economic Geology, 8, 140 (1913).

Regarding the reaction between cupric sulfide and silver salts Anthon[1] and Schuermann[2] report the formation of silver sulfide; whereas C. Palmer and E. S. Bastin[3] assert that metallic silver as well as silver sulfide is formed. It was therefore necessary to determine this reaction.

A very pure specimen of covellite from Butte, Montana (Cu 66.43%, S 33.28%, Fe 0.05%, SiO$_2$ 0.07%), and a chemically pure synthetic cupric sulfide were used. The very finely ground material was heated for several hours on the steam bath with solutions of silver nitrate and sulfate, respectively. The resulting substance was then filtered and washed   It proved to be silver sulfide. Dr. H. E. Merwin kindly examined it microscopically. He found it to be perfectly homogeneous and in neither case when natural or synthetic cupric sulfide was used, could he detect any metallic silver.

Substances resulting from the reaction of the silver salt upon cupric sulfide were analyzed. The results are given in Table I.

TABLE I.

Weight of cupric sulfide in g.	Silver found in the resulting substance.	Mol silver for each mol of cupric sulfide.	Remarks
0.3178	0 7216	2.01	Synthetic CuS treated with Ag$_2$SO$_4$
0.3184	0.7169	1 99	Synthetic CuS treated with AgNO$_3$
0.3164	0.7029	1.98	Natural CuS (Butte, Montana) treated with AgNO$_3$

One may see from this table that synthetic cupric sulfide acts exactly like the natural mineral and that the nature of the silver salt has no specific influence on the reaction. Further, that, when the reaction between cupric sulfide and silver salt solution takes place, each mol of cupric sulfide reacts with two mols of silver, as is necessary for the formation of silver sulfide. The reaction may therefore be written

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$
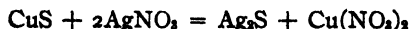
It was also shown in a different way that no metallic silver is formed by the reaction between cupric sulfide and silver nitrate, while the reaction between cuprous sulfide and silver nitrate gives equal quantities of silver, as metallic silver and as silver sulfide.

It is known that metallic silver can be dissolved in a solution of ferric nitrate. This reaction may be expressed as follows:[4]

$$Ag + Fe(NO_3)_3 \rightleftharpoons AgNO_3 + Fe(NO_3)_2$$
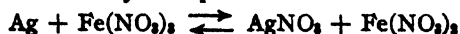
According to the thermochemical equation[5]

[1] *J. prakt. Chem.*, **10**, 355 (1837).
[2] *Ann.*, **249**, 326.
[3] *Loc. cit.*
[4] THIS JOURNAL, **34**, 1016 (1912).
[5] Landolt-Börnstein-Roth Tabellen.

$$Ag + Fe(NO_3)_3.Aq = AgNO_3.Aq + Fe(NO_3)_2.Aq - 172,300 \text{ cal.}$$

the equilibrium will be displaced from left to right with increase of temperature. An excess of ferric nitrate will also displace the equilibrium in the same direction, so that conditions are readily found, under which practically all the silver may be dissolved. It was found that a 6% solution of ferric nitrate (anhydrous) and a temperature of about 70° were well adapted to this purpose.

The substances resulting from the reaction of cuprous and cupric sulfide, respectively, with silver nitrate were now tested for the quantity of metallic silver they contained. Each was treated twice with the solution of ferric nitrate and filtered through a hot water funnel. The silver was then determined in the solution as well as in the residue. The results are given in Table II.

TABLE II.

Weight of original substance.	Silver extracted with ferric nitrate solution.	Silver in the residue.	Ratio of extracted silver to the silver in the residue.
0.3188 g. Cu$_2$S.............	0.4263	0.4292	0.993
0.3226 g. CuS.............	0.0096	0.7170	0.013

The last column in this table gives the ratio of silver found in the ferric nitrate extract to the silver found in the residue. It shows that in the case of cuprous sulfide this ratio, within the limits of the experimental error, is 1. This means that the substance resulting from the treatment of cuprous sulfide with silver nitrate contains equal amounts of silver as metallic silver and as silver sulfide, and confirms the above reaction, viz.,

$$Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2.$$

Treating the substance resulting from the reaction of cupric sulfide and silver nitrate with ferric nitrate, a small amount of silver was found in the extract as shown in the table. This amount (1.3% of the total silver) lies probably within the experimental errors and might be due to some decomposition of silver sulfide. This together with the previous experiments on this point, proves that no metallic silver was present and we can express the reaction between cupric sulfide and silver nitrate by the equation

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$
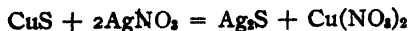
The different ways in which cuprous and cupric sulfide react with silver nitrate give us the possibility of determining each of them in a mixture of the two. After treating such a mixture with silver nitrate it would only be necessary to separate, in the resulting substance, the metallic silver from the silver sulfide, which we have previously seen can be accomplished by means of a ferric nitrate solution. The silver is then determined in the filtrate as well as in the residue. The amount of cuprous

sulfide is calculated from the silver found in the filtrate. The difference in silver found in the residue and in the filtrate serves for the calculation of the cupric sulfide. For, if the substance consisted only of cuprous sulfide we should find equal quantities of silver in the filtrate and in the residue (within the limit of experimental error), while if cupric sulfide was present, there would be more silver in the residue than in the filtrate and this excess would correspond to the amount of cupric sulfide in the mixture.

To make such a determination, conditions described below must be followed. The substance to be examined must be at least fine enough to pass through a 200 mesh (per linear inch) sieve. About 0.4–0.5 g. material are treated with 50 cc. of a 5% silver nitrate solution, which is added gradually with vigorous stirring. Most of the reaction takes place within a few minutes. To complete it, however, the covered beaker must be put on the steam bath for about 3 hrs. and the contents vigorously stirred at short intervals. The stirring is necessary because some of the material might otherwise be enveloped with metallic silver and silver sulfide and this small quantity might remain unchanged. After the reaction is complete the precipitate is filtered and washed by decantation till the filtrate no longer reacts with hydrochloric acid. The precipitate is then collected in the beaker and extracted two or three times with 40–50 cc. of a 6% solution of ferric nitrate (anhydrous). This operation is carried out at about 70°.[1] The extract is filtered each time through a hot

TABLE III.

	Original mixture in per cent.	Ratio found in per cent.	Difference.
Cu₂S..............	96.25	96.36	±0.11
CuS.............	3.75	3.64	
Cu₂S.............	93.80	92.50	+1.30
CuS.............	6.20	7.50	
Cu₂S.............	93.06	91.50	+1.56
CuS.............	6.94	8.50	
Cu₂S.............	84.76	83.70	+1.06
CuS.............	15.24	16.30	
Cu₂S.............	79.08	77.60	+1.48
CuS.............	20.92	22.40	
Cu₂S.............	45.07	45.36	±0.29
CuS.............	54.93	54.64	
Cu₂S.............	12.35	12.64	±0.29
CuS.............	87.65	87.36	
Cu₂S.............	10.43	10.31	+0.12
CuS.............	89.57	89.69	
Cu₂S.............	4.95	5.39	±0.44
CuS.............	95.05	94.61	
Cu₂S.............	1.66	2.96	±1.30
CuS.............	98.34	97.04	

[1] Higher temperature causes hydrolysis and precipitation.

water funnel and the residue is finally washed with hot water. To the filtrate nitric acid is then added until it becomes colorless. The silver is then precipitated and weighed as silver chloride. The residue is roasted, dissolved in nitric acid and the silver determined as silver chloride. The percentage of cuprous and cupric sulfide in the mixture is calculated from the quantities of silver chloride. Table III gives a number of such determinations. They were made with natural cuprous (Cu 79.67%, S 20.16%, Fe 0.14%, SiO$_2$ 0.06%) and cupric sulfides (given above).

As seen from these results the method is accurate within 1.5%, which may be regarded as satisfactory.

In this method the metallic silver alone may be determined and from this, if the original weight of the substance is known, both cuprous and cupric sulfide may be calculated. However, the assumption that the silver found is strictly proportional to the quantity of cuprous sulfide is not safe. It sometimes happens that, owing to insufficient stirring, a small part of the mixture (Cu$_2$S, CuS) does not react with silver nitrate. The absolute amount of cuprous sulfide that corresponds to the metallic silver would in such case be too low. But the occlusion probably affects cupric sulfide in a similar degree as it does cuprous sulfide. For that reason if both were determined, both would be too low while their percentages, calculated from the total weight found, would be correct. The data given in the last table under "found" were calculated in this way

Summary.

The reaction between cuprous sulfide and silver nitrate was confirmed in accordance with the equation:

$$Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2$$

It was found that silver sulfide only, and no metallic silver, is formed by the reaction between cupric sulfide and silver nitrate, the equation for this reaction being

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$
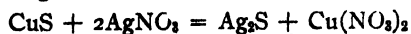
Based on the difference between these reactions a method is given for the determination of cuprous and cupric sulfide in mixtures of the two. The mixture is treated with silver nitrate and from the product the metallic silver is extracted by means of ferric nitrate. The amount of cuprous sulfide is calculated from the metallic silver, while the cupric sulfide is calculated from the difference between the silver in the silver sulfide and the metallic silver.

In mixtures containing the constituents in any proportion whatever the method was shown to be accurate within 1.5%.

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION,
WASHINGTON, D. C.

CORRECTION.

In the article on "Leakage Prevention by Shielding, Especially in Potentiometer Systems," by Walter P. White, which appeared in the October number of this year, on page 2018, 7th line from the bottom of the page, instead of: "arrangement described in connection with Fig. 7 of the previous paper on potentiometers," it should read: "arrangement described in connection with Section 4, (a) of the previous paper on potentiometers, page 1875."

THE PARTIAL VAPOR PRESSURES OF TERNARY MIXTURES OF TOLUENE, CARBON TETRACHLORIDE AND ETHYLENE BROMIDE.

By M. A. Rosanoff, John F. W. Schulze and R. A. Dunphy.

The measurements reported in this paper were carried out in connection with a study of fractional distillation with regulated stillheads.   In the case of binary mixtures, F. D. Brown[1] has shown that, if a saturated
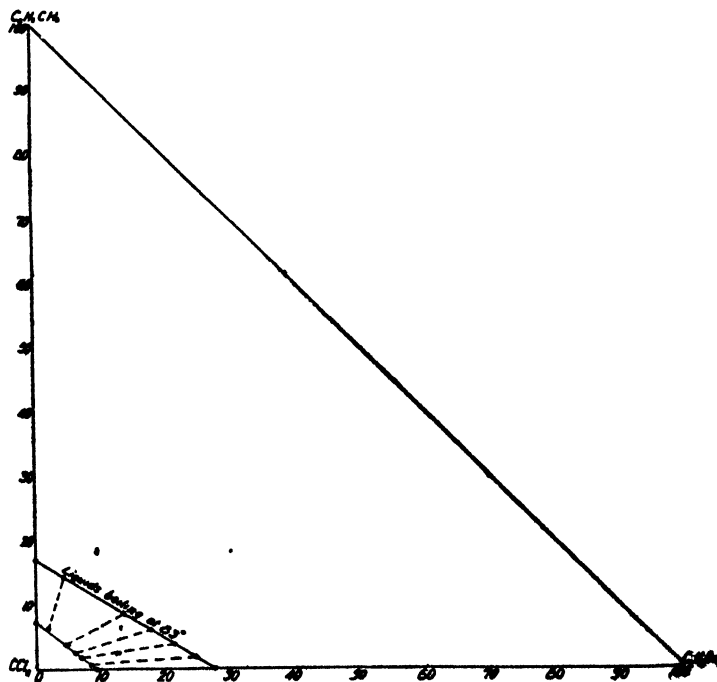
Fig 1.

[1] F. D. Brown, *Trans. Chem. Soc.*, 37, 49 (1880) and especially *Ibid.*, 39, 517 (1881).

vapor is partially condensed in a stillhead maintained at a constant temperature, the residual vapor escaping from the stillhead has a *constant composition, viz.,* the composition of the vapor given off by that liquid mixture which boils at the temperature of the stillhead. The effect of the regulated stillhead on vapors containing more than two components has never been investigated, and before such an investigation could be undertaken it was necessary to take two preliminary steps: (1) to work out a method by which consecutive fractions of a ternary distillate could be rapidly and accurately analyzed (2) with a view to discovering the law involved, to determine the partial pressures of the ternary mixtures of a suitable set of three substances, at the boiling points of the mixtures under ordinary atmospheric pressure.
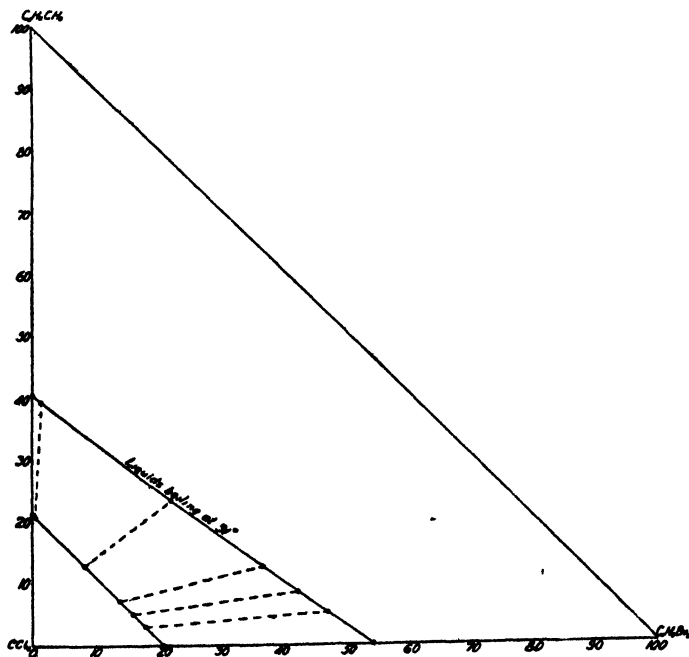
Fig 2.

Toluene, carbon tetrachloride, and ethylene bromide were chosen, because, on the one hand, their ternary boiling point surface is not complicated by either a maximum or a minimum; and because, on the other hand, they differ widely in their physical properties, so that their mixtures could be accurately analyzed by a physico-chemical method. The needed analytical method was worked out by one of us and fully described

in a separate communication.[1] We next undertook to determine the required partial pressures or, what is the same, the composition of the vapors in equilibrium with various mixtures of our three substances.

As to the method to be employed, there could be no hesitation. Von Zawidzki's[2] method, in which 1 cc. is distilled off from about 125 cc. of mixture, could not be used; our analytical procedure called for about 10 cc. of the liquid to be analyzed, and to obtain such a quantity of distillate without greatly affecting the composition of the original mixture, we should have had to use, in each single run. as much as 1 to 1.5 liters of mixture;
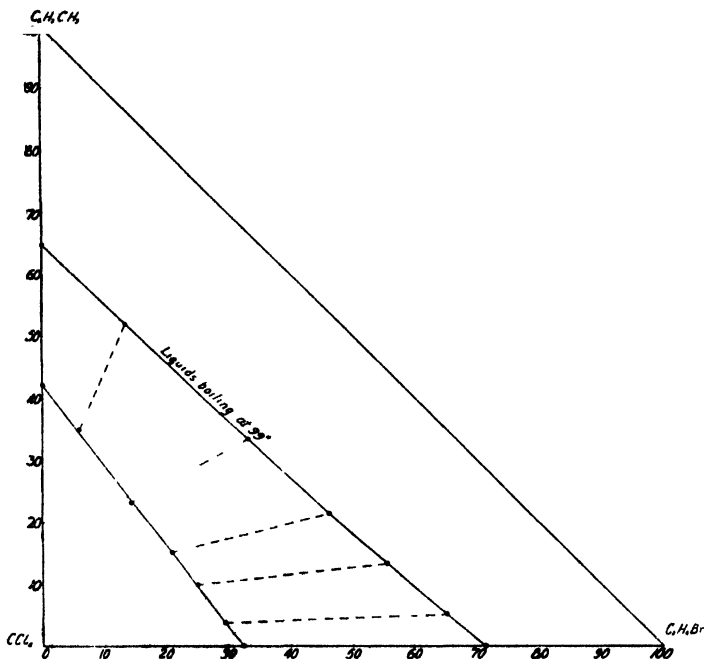
Fig. 3.

which was impracticable.   The method of Rosanoff, Lamb, and Breithut[3] could not be used as it would have been exceedingly difficult to produce a ternary saturated vapor of constant composition.   There remained the method described by Rosanoff, Bacon and White,[4] and this we found to work as well with ternary as it does with binary mixtures.

¹ Schulze, THIS JOURNAL, 36, 498 (1914).

² Von Zawidzki, Z. physik. Chem., 35, 129 (1900).

³ Rosanoff, Lamb and Breithut, THIS JOURNAL, 31, 448 (1909); Z. physik. Chem., 66, 349 (1909).

⁴ Rosanoff, Bacon and White, THIS JOURNAL, 36, 1803 (1914).

As in the case of binary mixtures, the method consisted simply in preparing a set of different mixtures of exactly known composition, subjecting each to distillation without reflux condensation, and analyzing consecutive fractions of the distillates. The amount of mixture employed each time was only 100 cc. The analyses were made by determining both the index of refraction and the density of each separate distillate. The treatment of the results was more laborious than with binary mixtures, owing to the fact that three-dimensional coördinates could not be conveniently employed. The method involves, namely, plotting the com-
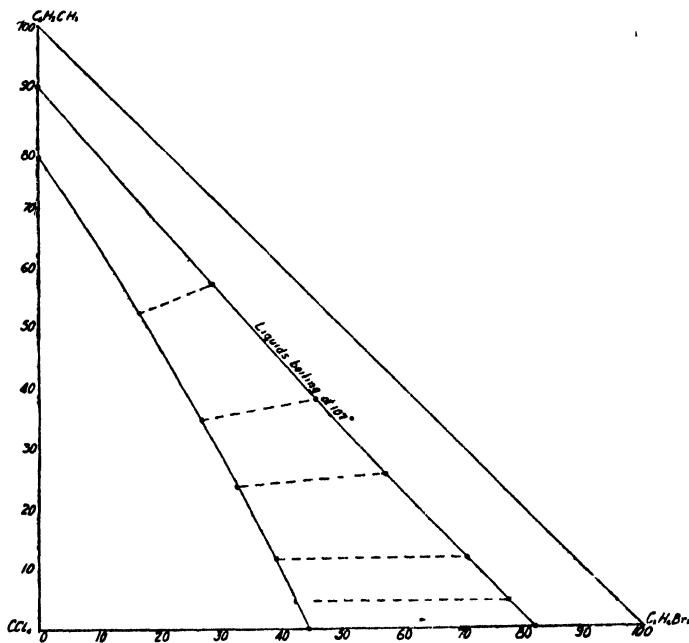
Fig 4.

position of the first fraction against the weight of that fraction, the composition that would result by mixing the first and second fractions, against the combined weight of those two fractions, then the combined composition of Fractions 1 + 2 + 3 against the combined weight of the three fractions, etc., and extending the resulting curve to where the weight of distillate is zero. The point thus attained by the curve would indicate the composition of the first infinitesimal amount of vapor evolved by the given mixture. In the case of ternary mixtures the composition would require two coördinate axes for its representation, while the corresponding weights require a third axis. To obtain the desired result with the aid

or ordinary cross-section paper, we had to resort to an indirect procedure, and it is this that involved some additional labor. We proceeded as follows: Having calculated the combined composition of Fractions 1 + 2, Fractions 1 + 2 + 3, etc., we ascertained, from Schulze's curves, the indices of refraction and the densities that these combined distillates would have. The indices and the densities were *separately* plotted against the weights. In this manner two separate plane curves were obtained, which, extended to where weight equals zero, indicated respectively, the refractive index and the density of the first infinitesimal quantity of distillate. The two physical properties revealed *the composition of that first infinitesimal distillate or, what is the same, of the vapor in equilibrium with the given ternary mixture.*
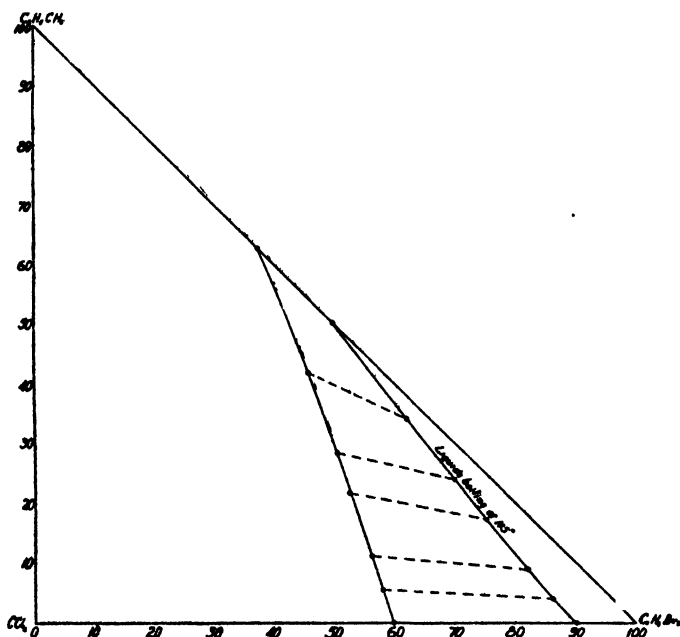
Fig. 5.

The measurements, as already stated, were undertaken as preliminary to a study of the regulated stillhead. For the purposes of that study it was necessary to learn what vapors are in equilibrium with the various ternary liquids boiling at least at some one temperature. We did this for five different temperatures, *viz.*, for 83°, 91°, 99°, 107°, and 115°. And for each of these temperatures we studied five different ternary mixtures and the two binary mixtures, all boiling at that temperature. The re-

sults, tabulated below, are graphically reproduced in Figs. 1 to 5. The system of coördinates used is an isosceles right-angled triangle, which is by far the most convenient for practical purposes. The length of each of the equal sides is 100. Each vertex represents one of the components in the pure state. Every point on a side represents a binary mixture. Any point within the triangle represents a ternary mixture: its perpendicular distance from each of the two equal sides measures the percentage of the component represented by the vertex opposite to that side, its distance from the hypothenuse, measured alone a line parallel to either of the two equal sides, represents the percentage of the third component. In each of our figures, the heavier curve is an isothermal, showing the compositions of the various mixtures boiling at the stated temperature; the lighter curve represents the composition of the vapors in equilibrium with those various liquids, the point for each liquid studied being connected by a tie-line with that representing the corresponding vapor.

The very same substances were used again that had been prepared and purified in working out the analytical method.[1]

In the tables below all percentages are *by weight*.

Numerical Results.

TABLE I.—FIRST MIXTURE OF BOILING POINT 83°   COMPOSITION OF THE MIXTURE:

83 00% CCl_4 + 17 00% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$

Distillate No	Weight of distillate	Spec vol	Refractive angle	% CCl	% C₆H₅CH₃	% C₂H₄Br₂
1	22 745	0 6693	44 442	92 35	7 65	0
2	22 647	0 6740	44 358	91 45	8.55	0
3	21 283	0 6827	44 192	89 8	10 2	0
4 .	21 367	0 6948	43 958	87 5	12 5	0
5	20 345	0 7171	43 567	83 3	16 7	0

Hence, composition of first infinitesimal amount of distillate 92 7% CCl_4 + 7.3% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$

TABLE II.—SECOND MIXTURE OF BOILING POINT 83°   COMPOSITION OF THE MIXTURE:

81 26% CCl_4 + 14 34% $C_6H_5CH_3$ + 4 40% $C_2H_4Br_2$

Distillate No.	Weight of distillate	Spec vol	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₆H₄Br₂
1	21 498	0 6610	44 417	91 25	6 75	2.0
2...1	24 456	0 6644	44 342	90 45	7 4	2 15
3 .	23 146	0 6713	44 158	88 7	8 8	2 5
4.. .	23 951	0 6815	43 900	86.1	10 85	3 05
5.......	20 611	0 7006	43 433	81 3	14 8	3 9

Hence, composition of first infinitesimal amount of distillate 91 8% CCl_4 + 6.3% $C_6H_5CH_3$ + 1.9% $C_2H_4Br_2$.

[1] Schulze, *loc. cit.*

TABLE III.—THIRD MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 77.76% CCl_4 + 8.64% $C_6H_5CH_3$ + 13.60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	22.152	0.6423	44.433	91.3	3.95	4.75
2.......	21.829	0.6437	44.367	90.65	4.35	5.0
3.......	20.959	0.6457	44.200	88.9	5.1	6.0
4.......	22.748	0.6487	43.967	86.5	6.1	7.4
5.......	21.876	0.6545	43.577	82.45	7.85	9.7

Hence, composition of first infinitesimal amount of distillate: 91.8% CCl_4 +3.75% $C_6H_5CH_3$ + 4.45% $C_2H_4Br_2$.

TABLE IV.—FOURTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 76.04% CCl_4 + 6.16% $C_6H_5CH_3$ + 17.80% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1..... .	24.000	0.6342	44.425	91.0	2.8	6.2
2.......	23.463	0.6345	44.350	90.2	3.1	6.7
3.......	23.548	0.6352	44.150	88 3	3 6	8.1
4.......	23.516	0.6366	43.867	85.5	4 5	10.0
5.......	23.181	0.6385	43.350	80.1	6.1	13.8

Hence, composition of first infinitesimal amount of distillate: 91.4% CCl_4 + 2.6% $C_6H_5CH_3$ + 6.0% $C_2H_4Br_2$.

TABLE V.—FIFTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 74.67% CCl_4 + 3.93% $C_6H_5CH_3$ + 21.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	25.734	0.6268	44.450	91.1	1.8	7.1
2.......	25.779	0.6265	44.350	90.0	2.0	8.0
3......	24.891	0.6255	44.117	87.8	2.5	9.7
4......	27.162	0.6241	43.750	84.1	3.1	12.8
5.......	23.929	0.6210	42.958	76.3	4.5	19.2

Hence, composition of first infinitesimal amount of distillate: 91.4% CCl_4 + 1.8% $C_6H_5CH_3$ + 6.8% $C_2H_4Br_2$.

TABLE VI.—SIXTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 73.42% CCl_4 + 1.88% $C_6H_5CH_3$ + 24.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	23.056	0.6198	44.417	90.5	0.8	8.7
2.......	24.124	0.6190	44.350	89.8	1.0	9.2
3.......	24.481	0.6169	44.150	87.9	1.1	11.0
4.......	24.350	0.6137	43.850	85.1	1.3	13.6
5.......	24.129	0.6079	43.283	79.4	1.9	18.7

Hence, composition of first infinitesimal amount of distillate: 90.8% CCl_4 + 0.8% $C_6H_5CH_3$ + 8.4% $C_2H_4Br_2$.

TABLE VII.—SEVENTH MIXTURE OF BOILING POINT 83°.   COMPOSITION OF THE MIX-
TURE: 72.30% CCl_4 + 0% $C_6H_5CH_3$ + 27.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$	% $C_2H_4Br_2$.
1.......	24.046	0.6136	44.425	90.4	0	9.6
2.......	24.461	0.6120	44.358	89.8	0	10.2
3.......	24.109	0.6087	44.150	87.7	0	12.3
4.......	24.539	0.6037	43.858	84.8	0	15.2
5.......	24.389	0.5941	43.250	79.2	0	20.8

Hence, composition of first infinitesimal amount of distillate: 90.7% CCl_4 + 0% $C_6H_5CH_3$ + 9.3% $C_2H_4Br_2$.

TABLE VIII.—FIRST MIXTURE OF BOILING POINT 91°.   COMPOSITION OF THE MIX-
TURE: 59.40% CCl_4 + 40.60% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	20.514	0.7473	43.083	77.6	22.4	0
2.......	20.846	0.7632	42.841	74.6	25.4	0
3.......	18.603	0.7895	42.467	69.6	30 4	0
4.......	19.676	0 8276	42.000	62 2	37.8	0
5.......	16.854	0.8931	41.283	50 0	50.0	0

Hence, composition of first infinitesimal amount of distillate: 78.6% CCl_4 + 21.4% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE IX.—SECOND MIXTURE OF BOILING POINT 91°.   COMPOSITION OF THE MIX-
TURE: 59.16% CCl_4 + 39.44% $C_6H_5CH_3$ + 1.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	20.816	0.7431	43.100	77 5	21.9	0.6
2.......	20.026	0.7582	42.867	74.6	24.8	0.6
3.......	18.790	0.7862	42.483	69.3	30.0	0.7
4.......	17 957	0.8175	42.067	63.3	36.0	0.7
5.......	16.585	0.8727	41.383	51.9	46.7	1 4

Hence, composition of first infinitesimal amount of distillate: 78.7% CCl_4 + 20.8% $C_6H_5CH_3$ + 0.5% $C_2H_4Br_2$.

TABLE X.—THIRD MIXTURE OF BOILING POINT 91°.   COMPOSITION OF THE MIXTURE:
54.67% CCl_4 + 23.43% $C_6H_5CH_3$ + 21.90% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	21.867	0.6855	43.150	78.2	13.5	8.3
2.......	21.606	0.6926	42.900	75.4	15.1	9.5
3.......	21 513	0.7048	42.433	69.5	18.2	12.3
4.......	20.527	0.7218	41.800	61.6	22.5	15.9
5.......	19.911	0.7475	40.650	46.3	29.8	23.9

Hence, composition of first infinitesimal amount of distillate: 79.1% CCl_4 + 12.8% $C_6H_5CH_3$ + 8.1% $C_2H_4Br_2$.

TABLE XI.—FOURTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 50.88% CCl₄ + 12.72% C₆H₅CH₃ + 36.40% C₂H₄Br₂.

No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	22.860	0.6448	43.150	78.25	7.5	14.25
2	23.822	0.6467	42.883	75.5	8.4	16.1
3	23.250	0.6494	42.275	68.9	10.5	20.6
4	23.362	0.6528	41.392	59.3	13.2	27.5
5	21.540	0.6541	39.783	41.9	17.6	40.5

Hence, composition of first infinitesimal amount of distillate: 79.0% CCl₄ + 7.2% C₆H₅CH₃ + 13.8% C₂H₄Br₂.

TABLE XII.—FIFTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 49.22% CCl₄ + 8.68% C₆H₅CH₃ + 42.10% C₂H₄Br₂.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	24.234	0.6289	43.117	77.8	5.3	16.9
2	24.755	0.6287	42.825	74.8	6.1	19.1
3	23.758	0.6274	42.183	68.5	7 4	24.1
4	23.339	0.6245	41.217	58.9	9.4	31.7
5	23.739	0.6150	39.300	40.4	12.4	47.2

Hence, composition of first infinitesimal amount of distillate: 79.0% CCl₄ + 5.1% C₆H₅CH₃ + 15.9% C₂H₄Br₂.

TABLE XIII.—SIXTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 47.88% CCl₄ + 5.32% C₆H₅CH₃ + 46.80% C₂H₄Br₂.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	24.777	0.6155	43.150	78.3	3.3	18.4
2	24.602	0.6138	42.850	75.3	3.7	21.0
3	24.453	0.6092	42.200	69.1	4.6	26.3
4	24.320	0.6011	41.133	59.1	5.8	35.1
5	24.511	0.5814	38.842	39.0	8.0	53.0

Hence, composition of first infinitesimal amount of distillate: 79.4% CCl₄ + 3.0% C₆H₅CH₃ + 17.6% C₂H₄Br₂.

TABLE XIV.—SEVENTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 45.80% CCl₄ + 0% C₆H₅CH₃ + 54.20% C₂H₄Br₂.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	28.555	0.5933	43.200	78.5	0	21.5
2	25.441	0.5878	42.843	75.2	0	24.8
3	25.965	0.5759	42.033	68.3	0	31.7
4	26.374	0.5551	41.517	56.0	0	44.0
5	28.389	0.5109	38.800	30.1	0	69.9

Hence, composition of first infinitesimal amount of distillate: 79.7% CCl₄ + 0% C₆H₅CH₃ + 20.3% C₂H₄Br₂.

TABLE XV.—FIRST MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 35.40% CCl_4 + 64.60% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol	Refractive angle.	% CCl₄	% C₆H₅CH₃.	% C₂H₄Br₂.
1.......	17.197	0.8610	41.600	56.0	44.0	0
2.......	16.973	0.8852	41.367	51.5	48.5	0
3.......	16.153	0.9281	40.967	43.5	56.5	0
4.......	16.029	0.9796	40.533	33.8	66.2	0
5.......	14.152	1.0410	40.067	22.3	77.7	0

Hence, composition of first infinitesimal amount of distillate: 57.7% CCl_4 + 42.3% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE XVI.—SECOND MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 34.64% CCl_4 + 51.96% $C_6H_5CH_3$ + 13.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃.	% C₂H₄Br₂.
1.......	18.596	0.8125	41.617	57.2	36.5	6.3
2.......	18.019	0.8333	41.300	51.8	40.8	7.4
3.......	17.841	0.8636	40.850	44.1	47.0	8.9
4.......	17.161	0.8994	40.333	34.0	54.8	11.2
5.......	16.080	0.9385	39.750	22.1	63.1	14.8

Hence, composition of first infinitesimal amount of distillate: 59.1% CCl_4 + 35.0% $C_6H_5CH_3$ + 5.9% $C_2H_4Br_2$.

TABLE XVII.—THIRD MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 33.50% CCl_4 + 33.50% $C_6H_5CH_3$ + 33.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃.	% C₂H₄Br₂.
1.......	19.716	0.7313	41.683	59.9	24.3	15.8
2.......	20.311	0.7443	41.275	54.4	27.5	18.1
3.......	18.853	0.7606	40.675	46.1	31.9	22.0
4.......	18.791	0.7778	39.950	35.3	36.9	27.8
5.......	18.188	0.7907	39.033	22.0	42.0	36.0

Hence, composition of first infinitesimal amount of distillate: 62.5% CCl_4 + 23.2% $C_6H_5CH_3$ + 14.3% $C_2H_4Br_2$.

TABLE XVIII.—FOURTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 32.16% CCl_4 + 21.44% $C_6H_5CH_3$ + 46.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl₄	% C₆H₅CH₃.	% C₂H₄Br₂.
1.......	21.482	0.6776	41.675	61.5	16.2	22.3
2.......	22.122	0.6832	41.200	55.9	18.4	25.7
3.......	21.453	0.6892	40.367	46.1	21.6	32.3
4.......	21.343	0.6932	39.333	34.0	25.0	41.0
5.......	21.138	0.6860	37.875	17.9	27.8	54.3

Hence, composition of first infinitesimal amount of distillate: 64.1% CCl_4 + 15.1% $C_6H_5CH_3$ + 20.8% $C_2H_4Br_2$.

TABLE XIX.—FIFTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIX-
TURE 31 15% CCl₄ + 13 35% C₆H₅CH₃ + 55 50% C₂H₄Br₂

Distillate No	Weight of distillate	Spec vol	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	23 196	0 6398	41 692	63 0	10 5	26 5
2	23 319	0 6399	41 083	56 7	12 0	31 3
3	23 195	0 6388	40 142	47 0	14 0	39 0
4	23 467	0 6303	38 600	31 8	16 6	51 6
5	24 275	0 6108	36 683	14 8	17 9	67 3

Hence, composition of first infinitesimal amount of distillate 65 0% CCl₄ + 10 0% C₆H₅CH₃ + 25 0% C₂H₄Br₂

TABLE XX.—SIXTH MIXTURE OF BOILING POINT 99° COMPOSITION OF THE MIX
TURE 29 67% CCl₄ + 5 23% C₆H₅CH₃ + 65 10% C₂H₄Br₂

Distillate No	Weight of distillate	Spec vol	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	25 059	0 5987	41 650	64 3	4 3	31 4
2	26 007	0 5920	40 875	57 2	5 0	37 8
3	26 686	0 5792	39 517	45 6	6 0	48 4
4	26 811	0 5559	37 200	27 1	7 3	65 6
5	26 210	0 5265	34 617	10 2	7 1	82 7

Hence, composition of first infinitesimal amount of distillate 66 7% CCl₄ + 4 0% C₆H₅CH₃ + 29 3% C₂H₄Br₂

TABLE XXI.—SEVENTH MIXTURE OF BOILING POINT 99° COMPOSITION OF THE
MIXTURE 28 55% CCl₄ + 0% C₆H₅CH₃ + 71 45% C₂H₄Br₂

Distillate No	Weight of distillate	Spec vol	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	26 418	0 5709	41 650	65 3	0	34 7
2	26 960	0 5571	40 650	57 2	0	42 8
3	28 091	0 5350	38 900	44 1	0	55 9
4	28 907	0 5006	35 817	23 9	0	76 1
5	31 107	0 4707	32 667	6 7	0	93 3

Hence, composition of first infinitesimal amount of distillate 67 6% CCl₄ + 0% C₆H₅CH₃ + 32 4% C₂H₄Br₂

TABLE XXII.—FIRST MIXTURE OF BOILING POINT 107° COMPOSITION OF THE
MIXTURE 9 90% CCl₄ + 90 10% C₆H₅CH₃ + 0% C₂H₄Br₂

Distillate No	Weight of distillate	Spec vol	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1	14 330	1 0549	39 967	19 6	80 4	0
2	13 999	1 0760	39 850	15 7	84 3	0
3	14 195	1 0941	39 733	12 3	87 7	0
4 ..	14 029	1 1144	39 600	8 5	91 5	0
5 ..	14 262	1 1368	39 483	4 2	95 8	0

Hence, composition of first infinitesimal amount of distillate. 21 5% CCl₄ + 78 5% C₆H₅CH₃ + 0% C₂H₄Br₂

TABLE XXIII.—SECOND MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE
MIXTURE: 14.32% CCl_4 + 57.28% $C_6H_5CH_3$ + 28.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	16.873	0.8820	40.017	30 0	53.2	16.8
2.......	17.085	0.8964	39.742	24.7	·56.5	18.8
3.......	16.437	0.9099	39.400	18.2	59.9	21.9
4.......	16.921	0.9175	39.050	12.0	62.5	25.5
5.......	15.999	0.9126	38.633	5.5	63.4	31.1

Hence, composition of first infinitesimal amount of distillate: 32.1% CCl_4 + 51.5%
$C_6H_5CH_3$ + 16.4% $C_2H_4Br_2$.

TABLE XXIV.—THIRD MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE
MIXTURE: 16.32% CCl_4 + 38.08% $C_6H_5CH_3$ + 45.60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec vol.	Refractive angle.	% CCl_4	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	19.324	0.7752	40.017	36.4	36.2	27.4
2.......	19.358	0.7841	39.583	30.5	39.0	30 5
3.......	19.413	0.7904	39.017	22 0	41.9	36 1
4.......	19.227	0.7874	38.350	13.0	43.5	43.5
5.......	19.264	0 7698	37.683	5.8	42.8	51.4

Hence, composition of first infinitesimal amount of distillate: 38.6% CCl_4 + 34.8%
$C_6H_5CH_3$ + 26.6% $C_2H_4Br_2$.

TABLE XXV.—FOURTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE
MIXTURE: 17.12% CCl_4 + 25.68% $C_6H_5CH_3$ + 57.20% $C_2H_4Br_2$

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	21.184	0.7042	39.967	40.6	25.0	34.4
2.......	20.802	0.7079	39.358	33.1	27 3	39.6
3.......	21.126	0.7067	38.592	24.0	29.3	46.7
4.......	21.185	0.6994	37.700	15.1	30.5	54.4
5.......	21.820	0.6780	36.750	5.9	29.7	64.4

Hence, composition of first infinitesimal amount of distillate: 43.9% CCl_4 + 23.7%
$C_6H_5CH_3$ + 32.4% $C_2H_4Br_2$.

TABLE XXVI.—FIFTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE
MIXTURE: 17.58% CCl_4 + 11.72% $C_6H_5CH_3$ + 70.75% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4	% $C_6H_5CH_3$	% $C_2H_4Br_2$
1.......	24.002	0.6211	39.850	45.2	12.2	42.6
2.......	24.133	0.6153	38.858	35.9	13.5	50.6
3....,...	24.510	0.6039	37.600	24.7	14.6	60.7
4.......	24.710	0.5860	36.117	12.9	14.9	72.2
5.......	25.360	0.5607	34.733	4.6	13.3	82.1

Hence, composition of first infinitesimal amount of distillate: 49.3% CCl_4 + 11.6%
$C_6H_5CH_3$ + 39.1% $C_2H_4Br_2$.

TABLE XXVII.—SIXTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 17.84% CCl_4 + 4.46% $C_6H_5CH_3$ + 77.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$
1	26.187	0.5756	39.817	48.5	4.8	46.7
2	25.844	0.5622	38.500	38.0	5.4	56.6
3	27.001	0.5433	36.708	24.7	6.0	69.3
4	28.328	0.5201	34.650	11.5	5.9	82.6
5	29.894	0.4986	33.067	3.3	4.8	91.9

Hence, composition of first infinitesimal amount of distillate: 53.1% CCl_4 + 4.6% $C_6H_5CH_3$ + 42.3% $C_2H_4Br_2$.

TABLE XXVIII.—SEVENTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 18.00% CCl_4 + 0% $C_6H_5CH_3$ + 82.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol	Refractive angle	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$
1	28.039	0.5459	39.750	50.5	0	49.5
2	26.919	0.5256	38.083	38.7	0	61.3
3	28.723	0.5007	35.817	24.0	0	76.0
4	29.234	0.4769	33.375	10.1	0	89.9
5	31.172	0.4637	31.850	2.4	0	97.6

Hence, composition of first infinitesimal amount of distillate: 55.5% CCl_4 + 0% $C_6H_5CH_3$ + 44.5% $C_2H_4Br_2$.

TABLE XXIX.—FIRST MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 0% CCl_4 + 50.40% $C_6H_5CH_3$ + 49 60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4	% $C_6H_5CH_3$	% $C_2H_4Br_2$.
1	17.144	0.8920	38.175	0	61.9	38.1
2	18.419	0.8763	38.083	0	59.6	40.4
3	17.651	0.8587	37.950	0	57.1	42.9
4	23.047	0.8307	37.750	0	53.1	46.9
5	18.346	0.7881	37.392	0	47.0	53.0

Hence, composition of first infinitesimal amount of distillate: 0% CCl_4 + 62.9% $C_6H_5CH_3$ + 37.1% $C_2H_4Br_2$.

TABLE XXX.—SECOND MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 3.81% CCl_4 + 34.29% $C_6H_5CH_3$ + 61.90% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1	18.090	0.7744	38.083	10.6	42.3	47.1
2	19.274	0.7667	37.792	7.6	41.9	50.5
3	18.998	0.7340	37.467	5.0	40.6	54.4
4	21.530	0.7340	37.100	3.0	38.3	58.7
5	21.960	0.7016	36.600	1.0	34.2	64.8

Hence, composition of first infinitesimal amount of distillate: 12.3% CCl_4 + 42.1% $C_6H_5CH_3$ + 45.6% $C_2H_4Br_2$.

TABLE XXXI.—THIRD MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE
MIXTURE: 6.00% CCl_4 + 24.00% $C_6H_5CH_3$ + 70.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.171	0.6995	37.983	17.5	29.9	52.6
2.......	21.543	0.6921	37.450	11.1	31.5	57.4
3.......	21.509	0.6792	36.908	7.6	29.4	63.0
4.......	21.668	0.6599	36.333	3.9	27.6	68.5
5.......	23.061	0.6315	35.683	1.4	24.1	74.5

Hence, composition of first infinitesimal amount of distillate: 21.2% CCl_4 + 28.5%
$C_6H_5CH_3$ + 50.3% $C_2H_4Br_2$.

TABLE XXXII.—FOURTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE
MIXTURE: 7.44% CCl_4 + 17.36% $C_6H_5CH_3$ + 75.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	20.857	0.6530	37.983	22.8	22.0	55.2
2.......	21.763	0.6437	37.233	15.8	22.4	61.8
3.......	22.558	0.6316	36.517	10.1	22.0	67.9
4.......	22.841	0.6134	35.758	5.0	20.7	74.3
5.......	23.669	0.5887	35.017	2.0	17.9	80.1

Hence, composition of first infinitesimal amount of distillate: 25.7% CCl_4 + 21.8%
$C_6H_5CH_3$ + 52.5% $C_2H_4Br_2$.

TABLE XXXIII.—FIFTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE
MIXTURE: 8.88% CCl_4 + 8.87% $C_6H_5CH_3$ + 82.25% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.412	0.5880	37.750	28.1	11.5	60.4
2.......	25.717	0.5756	36.600	19.1	11.9	69.0
3.......	25.136	0.5601	35.425	11.0	11.6	77.4
4.......	26.253	0.5422	34.367	4.9	10.6	84.5
5.......	27.417	0.5219	33.467	1.4	8.5	90.1

Hence, composition of first infinitesimal amount of distillate: 32.7% CCl_4 + 11.2%
$C_6H_5CH_3$ + 56.1% $C_2H_4Br_2$.

TABLE XXXIV.—SIXTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE
MIXTURE: 9.66% CCl_4 + 4.14% $C_6H_5CH_3$ + 86.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	26.402	0.5517	37.567	30.9	5.6	63.5
2.......	27.329	0.5351	36.067	20.5	5.8	73.7
3.......	28.942	0.5171	34.525	11.4	5.4	83.2
4.......	28.835	0.5006	33.250	4.5	4.7	90.8
5.......	30.973	0.4870	32.450	0.8	3.7	95.5

Hence, composition of first infinitesimal amount of distillate: 36.5% CCl_4 + 5.5%
$C_6H_5CH_3$ + 58.0% $C_2H_4Br_2$.

TABLE XXXV.—SEVENTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE
MIXTURE: 10.00% CCl₄ + 0% C₆H₅CH₃ + 90.00% C₂H₄Br₂.

Distillate No	Weight of distillate.	Spec. vol.	Refractive angle	% CCl₄	% C₆H₅CH₃	% C₂H₄Br₂
1......	28.588	0 5160	37.233	32.7	0	67.3
2.......	29.331	0.4956	35.333	21 1	0	78.9
3.......	29.414	0 4780	33.508	11 5	0	88.5
4.......	31.646	0.4665	32.200	4 6	0	95.4
5......	31.456	0 4611	31 583	1.3	0	98.7

Hence, composition of first infinitesimal amount of distillate: 40.0% CCl₄ + 0%
C₆H₅CH₃ + 60 0% C₂H₄Br₂.

TABLE XXXVI.—SUMMARY.

Temp	Mixture	Composition of liquid.			Composition of vapor		
		% CCl₄	% C₇H₈	% C₂H₄Br₂	% CCl₄	% C₇H₈	% C₂H₄Br₂
83°	1	83 00	17 00	0	92 7	7.3	0
83°	2	81.26	14 34	4 40	91 8	6 3	1 9
83°	3	77.76	8 64	13 60	91 8	3 75	4.45
83°	4	76 04	6 16	17 800	91 4	2 6	6 0
83°	5	74 67	3.93	21.40	91.4	1.8	6.8
83°	6	73 42	1.88	24.70	90 8	0.8	8.4
83°	7	72 30	0	27.70	90 7	0	9.3
91°	1	59 40	40 60	0	78.6	21 4	0
91°	2	59 16	39 44	1 4	78 7	20 8	0 5
91°	3	54 67	23.43	21 90	79 1	12 8	8 1
91°	4	50 88	12 72	36 40	79 0	7.2	13.8
91°	5	49.22	8.68	42.10	79 0	5 1	15 9
91°	6	47 88	5.32	46 80	79 4	3.0	17 6
91°	7	45.80	0	54.2	79.7	0	20.3
99°	1	35.40	64 60	0	57.7	42.3	0
99°	2	34.64	51 96	13 40	59. 1	35 0	5.9
99°	3	33.50	33.50	33.00	62 5	23 2	14.3
99°	4	32.16	21.44	46 40	64.1	15.1	20.8
99°	5	31.15	13.35	55.50	65.0	10.0	25.0
99°	6	29 67	5.23	65.10	66.7	4.0	29.3
99°	7	28.55	0	71.45	67.6	0	32.4
107°	1	9.90	90 10	0	21.5	78.5	0
107°	2	14.32	57.28	28 40	32.1	51.5	16.4
107°	3	16.32	38 08	45.60	38.6	34.8	26.6
107°	4	17.12	25 68	57.20	43.9	23.7	32.4
107°	5	17.58	11 72	70.75	49.3	11.6	39.1
107°	6	17.84	4.46	77 70	53.1	4.6	42.3
107°	7	18 00	0	82.0	55.5	0	44 5
115°	1	0	50.40	49.60	0	62.9	37.1
115°	2	3.81	34 29	61.90	12.3	42.1	45.6
115°	3	6.00	24.00	70.00	21.2	28.5	50.3
115°	4	7.44	17.36	75.20	25.7	21.8	52.5
115°	5	8.88	8.87	82.25	32.7	11.2	56.1
115°	6	9.66	4.14	86.20	36.5	5.5	58.0
115°	7	10.00	0	90.00	40.0	0	60.0

In conclusion, it is a duty to state that the cost of this investigation has been defrayed out of a grant from the Rumford Fund of the American Academy, for which we express our thanks to the Rumford Committee.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

SUBSTITUTION IN THE BENZENE NUCLEUS.

BY A. F. HOLLEMAN.

A few years ago, I showed[1] that none of the hypotheses proposed to explain the phenomena of substitution in benzene nucleus , are able to give a satisfactory explanation of the facts. Since then, H. S. Fry, in a series of papers,[2] published a new hypothesis and was able to explain some of the phenomena observed by means of it, e. g., the fact that, in the rearrangement of phenyl acetyl nitrogen chloride $C_6H_5NCl.COCH_3$ and similar compounds, the halogen enters only in positions ortho or para to the nitrogen atom.

However, on studying this hypothesis more closely it seems to me that there are so many objections against it, that it cannot be accepted. I venture to present the most important ones in the following lines.

1. Fry admits that benzene has the structure of Fig. 1, based on Thomson's electronic theory of linking of the atoms. As he observes, this formula indicates the possibility of two isomeric compounds C_6H_5X, whereas no such isomers have been found thus far. In order to explain this, he assumes either that one of the two isomers ("electromers"), e. g., of chlorobenzene is unstable under ordinary physical conditions, or that monochlorobenzene is an equilibrium mixture of two tautomeric electromers. It seems to me that serious objections may be made against both of these auxiliary hypotheses. With regard to the first one; admitting $C_6H_5\overset{-}{Cl}$ to be stable, $C_6H_5\overset{+}{Cl}$ would be unstable. But in $o\text{-}C_6H_4Cl_2$ and $p\text{-}C_6H_4Cl_2$, where one Cl-atom is negative and the other positive, we have perfectly stable compounds. On the other hand, if monochlorobenzene is a mixture of $C_6H_5\overset{-}{Cl}$ and $C_6H_5\overset{+}{Cl}$, the nitration of such a mixture ought to give a mixture of o- and p-chloronitrobenzene (derived from $C_6H_5\overset{-}{Cl}$) and of m-chloronitrobenzene (derived from $C_6H_5\overset{+}{Cl}$), since—according to Fry—"substituents of the same sign occupy positions which
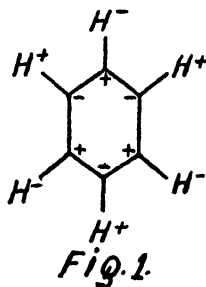
Fig. 1.

[1] "Die direkte Einführung von Substituenten in den Benzolkern," p. 263.

[2] THIS JOURNAL, 34, 664 (1912); 36, 248, 262 (1914); see also Z. physik. Chem., 76, 385 (1910).

are meta to each other, and substituents of opposite sign will occupy positions either ortho or para to each other." Now, I have been able to prove that in the nitration of chlorobenzene no trace of *m*-compound is formed, since the eutectic point of an artificial mixture of *p*- and *o*-chloronitrobenzene coincides with the eutectic point of the nitration product of chlorobenzene.

2. It can be proven in still another way that Fry's rule, just mentioned, with regard to the position taken by a new substituent, cannot be correct. Fry maintains that the iodine is positive in iodobenzene, since it is formed from sodium benzoate and iodine chloride, the latter having the formula $\overset{-}{Cl}$—$\overset{+}{I}$. But iodobenzene also yields *p*- and *o*-compounds on nitration, just as the other halogen-benzenes, though in these the halogen is admitted to have a negative charge. For the rest, it is somewhat striking, that Fry admits on p. 252, *l. c.*, that chlorobenzene has the formula $C_6H_5\overset{-}{Cl}$, whereas he declares on p. 264, that "it has been impossible so far to prove directly, whether the chlorine atom in monochlorobenzene is positive or negative."

3. According to Fry, "the radical SO_3H in phenylsulfonic acid may function either positively or negatively." He deduces this from the fact that this acid yields benzene on heating with water, but phenol on melting with alkali. But, since in *o*- and *p*-phenylene disulfonic acid one SO_3H should be positive when the other is negative, these acids should yield phenol exclusively on melting with alkali. In reality they yield pyrocatechol and hydroquinol.

4. The formula of *p*-chlorotoluene and *p*-chlorobromobenzene must be as is indicated in Fig. 2, according to the hypothesis of Fry.
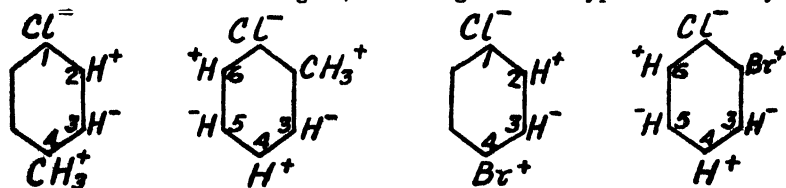
Fig. 2.

If his rule were correct, we should expect that in the nitration of the two *p*-compounds the group nitro+ (because nitric acid must be $\overset{-}{HO}.\overset{+}{NO_2}$) should only take position 2, because the H-atom placed there, must be positive. However, by researches executed in my laboratory by Wibaut[1] and by Heineken,[2] it is proved, that in both cases considerable

[1] *Recueil*, 32, 244 (1913).
[2] Not yet published.

quantities of both of the isomers 2 and 3 are obtained. In the case of *o*-chlorotoluene and *o*-chlorobromobenzene, Wibaut[1] proved for the first substance, that the nitration yields all the four possible mononitro compounds in considerable quantity, and for the second substance, I have proved that the nitration product contains almost equal quantities of the nitro products 4 and 5,[2] though Fry's rule predicts the formation of only the isomers 4 and 6. It is evident, that these objections would undergo no change, if all the signs admitted here for the substituents were the reverse.

5. Fry's explanation of the fact that the chlorination of nitrobenzene yields *m*-nitrochlorobenzene, can neither be accepted. He supposes that $\overset{-}{H}O.\overset{+}{C}l$ is the chlorinating agent "since absolutely anhydrous chlorine does not react with anhydrous reagents." However, this introduction of chlorine is only possible, when a large quantity of $SbCl_5$ is added ($^1/_5$ of the weight of the nitrobenzene). All traces of water must be taken away by it. The only plausible explanation is, that $SbCl_5$ is formed, which transports the chlorine to the nitrobenzene. As there can be little doubt that $SbCl_5$ is $\overset{-}{S}b\overset{+}{C}l_5$ (always according to the views of Fry) chlorine ought to replace an *o*- or *p*-H-atom in $C_6H_5NO_2$, when NO_2 in it is positive.

6. The substitution of chlorine in *o*- and *p*-chloronitrobenzene by OH is explained very well by Fry's hypothesis, admitting for the formulas of these compounds $\overset{-}{C}l.C_6H_4.\overset{+}{N}O_2(p\text{-}o)$; for the negative OH is now able to change places with the negative Cl. The fact that chlorine in *m*-chloronitrobenzene cannot be replaced is also explained in this way, since it has the formula $\overset{+}{C}l.C_6H_4.\overset{+}{N}O_2(m)$. Admitting this explanation, one Cl should also be replaceable by OCH_3 in *o*- and *p*-dichlorobenzene, $\overset{-}{C}l.C_6H_4.\overset{+}{C}l$, but not in *m*-dichlorobenzene, $\overset{-}{C}l.C_6H_4.\overset{+}{C}l$ (or $\overset{+}{C}l.C_6H_4.\overset{+}{C}l$). However, de Mooy[2] has proved in my laboratory, that the latter also reacts with sodium methylate, and that the velocity of this reaction is even greater than for the *p*- and *o*-isomers, one Cl-atom being replaced in all three compounds.

I wish, finally, to call attention to two further points. In the first place, it would probably be very difficult to designate what charge a given substituent has. In most cases it might as well be positive as negative. This naturally causes a great uncertainty in the explanation of the reactions. In the second place, I might direct the attention on the consequences of the hypothesis in the case of open carbon chains. For these, it leads to the formula $\overset{+}{C}\!-\!\overset{-+}{C}\!-\!\overset{-+}{C}\!-\!\overset{-}{C}$ ..., for the linking of the

[1] *Loc. cit.*
[2] Not yet published.

C-atoms comes about by C-atom 1 giving off an electron to C-atom 2, this sending off an electron in its turn to C-atom 2, and so on. This must cause the C-atoms at both ends of an open chain to have opposite signs. This would involve the consequence that the Br-atoms, *e. g.*, in a polymethylene dibromide, ought to show a different behavior, which is also in contradiction with the experimental facts.

CHEMICAL LABORATORY, UNIVERSITY OF AMSTERDAM.

THE ADDITION COMPOUNDS OF ORGANIC SUBSTANCES WITH SULFURIC ACID.

BY JAMES KENDALL AND CLIFFORD D. CARPENTER [1]

The treatment of aromatic organic substances with sulfuric acid, resulting in the formation of condensation products (sulfonic acids), is a well-known and widely-applied reaction. In a recent communication[2] the opinion was expressed that, in such condensations, the formation of addition compounds between the reacting substances may represent an intermediate stage of the process. The same view has been repeatedly advanced in the past, notably by Kekulé,[3] van't Hoff,[4] Michael,[5] and Guye.[6] Very little *systematic* evidence, however, has been brought forward in its support, save in the work of Menschutkin,[7] on the addition compounds of organic substances with inorganic salts, illustrating an intermediate phase of Friedel and Craft's reaction. The recent papers of Baume[8] and his pupils, on systems containing substances of very low freezing point, are also of importance.

Sulfonation is a vigorous reaction, induced by the application of heat. Of the mechanism of the process we know practically nothing, except that it is complex and probably consists of several distinct stages. Since, at the high temperatures employed, the reaction is rushed through all of these without a stop, no information has been obtained regarding possible intermediate products. Hoogewerff and van Dorp[9] have iso-

[1] The work presented in this paper forms the basis of a dissertation submitted by Clifford D. Carpenter to the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kendall, THIS JOURNAL, 36, 1722 (1914).

[3] Kekulé, *Ann.*, 106, 129 (1858).

[4] Van't Hoff, *Ansichten über organische Chemie*, I, 225, 244.

[5] Michael, THIS JOURNAL, 32, 1001 (1910).

[6] Guye, *J. chim. phys.*, 8, 119 (1910).

[7] Menschutkin, *J. chim. phys.*, 9, 538 (1911).

[8] Baume, *J. chim. phys.*, 12, 212 (1914).

[9] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, 18, 211 (1899); 21, 353 (1902).

lated some addition compounds of organic substances with sulfuric and phosphoric acids, but a *complete* examination has been made of no single system.

In the present investigation, the freezing point method previously described[1] is applied to the general study of sulfonation. The components are mixed at as low a temperature as possible and the mixture *frozen* instead of *heated;* in this way addition compounds, if formed, are at once isolated. The freezing point (temperature of *incipient solidification*) of a mixture of known composition gives us a point on the temperature-composition curve of the system, and from a series of mixtures of varying composition the complete diagram is obtained. In this diagram a break in the curve corresponds to a change in the solid phase crystallizing from the solution; a maximum point on the curve indicates a compound. At such a maximum point the mixture completely solidifies at constant temperature. The position of the maximum on the axis of molecular composition gives the formula of the compound; the sharpness of the curve around the maximum shows the relative extent of dissociation of the compound into its components. Fuller details of the experimental method followed, and of the interpretation of the diagrams obtained will be found on reference to the previous papers cited above.

The first class of substances examined consisted of the normal aromatic acids (benzoic acid and its homologs). It has already been shown[2] that these substances give addition compounds with stronger *organic* acids. In such systems the acidic properties of the weaker acid are suppressed and basic (unsaturated) properties are induced in the characteristic carbonyl group, the reaction taking place as follows:

$$R—C=O\overset{+}{\underset{|}{}} \;+\; HX \rightleftharpoons R—C=O\overset{X}{\underset{H}{<}}$$
$$\underset{OH}{}\qquad\qquad\qquad\underset{OH}{}$$
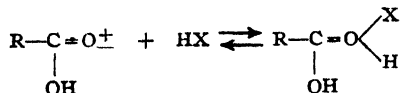
The compounds formed are consequently to be regarded as true oxonium salts. It will be obvious that the same reaction should apply if the stronger acid of the system is *inorganic, e. g.,* sulfuric acid. The primary dissociation of this acid is monobasic, hence the compounds obtained should be of the general type indicated above, $R.COOH,H_2SO_4$. However, 'the secondary dissociation of sulfuric acid also involves the possibility of addition compounds of the type $2R.COOH,H_2SO_4$.

The experimental results obtained showed that the reaction proceeds exactly as expected, addition compounds of both types being isolated. The investigation was therefore extended to include other classes of organic substances containing the characteristic $>C=O\overset{+}{\underset{-}{}}$ group, namely

[1] Kendall, This Journal, **36**, 1222 (1914).
[2] *Ibid.*, **36**, 1722 (1914).

aliphatic acids, aldehydes, ketones and anhydrides. All of these gave addition products with sulfuric acid. The action of sulfuric acid on phenols was also examined, with significant results. The complete list of substances studied is given below:

Aromatic acids.	Aliphatic acids.	Phenols
1. Benzoic	10. Chloroacetic	15. Phenol
2. o-Toluic	11. Trichloroacetic	16. o-Cresol
3. m-Toluic	12. Crotonic	17. p-Cresol
4. p-Toluic	13. α-Chlorocrotonic	18. p-Xylenol
5. α-Toluic	14. Glutaric	19. p-Xylenol
6. Salicylic		20. Thymol
7. o-Nitrobenzoic		21. o-Nitrophenol
8. Cinnamic		22. m-Nitrophenol
9. Mandelic		23. p-Nitrophenol

Aldehydes.	Ketones	Anhydrides.
24. p-Oxybenzaldehyde	28. Acetophenone	32. Benzoic
25. p-Nitrobenzaldehyde	29. Benzophenone	33. Succinic
26. Vanillin	30. Benzil	34. Phthalic
27. Piperonal	31. Dimethylpyrone	35. Coumarin

Experimental.

Pure sulfuric acid (100% H_2SO_4) was obtained by mixture of samples of higher and lower concentration, respectively. The acid of lower concentration employed was J. T. Baker's "Acid sulfuric, C. P. 95.6–96.4%," that of higher concentration was prepared from this by careful addition of Baker and Adamson's "Sulfuric acid, C. P. Fuming. ($H_2S_2O_7$)." The 100% acid thus obtained was standardized gravimetrically by the barium sulfate method. A more accurate criterion of its purity, however, was directly available in a determination of its freezing point, since a change in concentration of 0 1% corresponds to a difference of 0 6° in the point of fusion. The acid used throughout the investigation froze at 10.3–10.4°. This compares favorably with the values found by other observers,[1] when it is remembered that the acid could not be completely safeguarded from traces of moisture during the determinations. Contact with the outer air was made as short as possible by delivering the acid into the freezing point tube from a Grethan pipet.

The organic substances employed were mostly pure Kahlbaum specimens with satisfactory points of fusion. Only in a few cases was special purification necessary.

The experimental difficulties involved in the examination of the systems considered in the present paper were much greater than those encountered in previous work, and the method of procedure was necessarily

[1] Pickering, *J. Chem. Soc.*, **57**, 331 (1890) obtained 10.35° as the point of fusion. A slightly higher value—10.43° to 10.45°—was found by Lichty (THIS JOURNAL, **30**, 1842 (1908)).

slightly modified to reduce them as much as possible. In the first place, all solutions with low temperatures of fusion became very viscous and hard to stir. What little stirring could be done produced in the liquid a mass of air bubbles, difficult to distinguish from minute crystals, hence the solution never became perfectly clear and the freezing point appeared very indeterminate. In such systems each point was repeated several times and after considerable practice the exact temperature of fusion could be fixed. Secondly, almost all mixtures exhibited supercooling to a marked degree. So long as the freezing point curve of one of the components was being followed, solidification could be induced by the addition of a minute crystal of this component, but nothing could be done in cases where, a compound being expected, the mixture persistently hardened to a glassy mass without crystallization. Finally, certain of the systems (especially phenols) gave dark-colored solutions, in which it was very difficult to determine the presence of solid phase, although a yellow flame set behind the tube proved of some help.

Pure sulfuric acid fumes on exposure to the air, even at ordinary temperatures, and tends to lose SO_3. This was not, however, a cause of difficulty in the systems considered in the present paper, since the addition of the second component, with the consequent formation of compounds in the solution, considerably reduces this tendency to decomposition. Even at temperatures above 100° (where little sulfuric acid was present) no indications of evolution of sulfur trioxide or water from the mixtures were obtained.

Sulfonation itself rarely took place at the temperature of experiment.[1] In cases where sulfonation did proceed rapidly, the fact could at once be recognized by the presence of condensed water on the exposed portion of the tube. Such systems were not examined further. It is quite certain that the compounds isolated by freezing, described in the following pages, are addition and not sulfonation products,[2] for the sulfonic acids decompose on fusion and have no definite freezing points. Also the maximum points on the curves always correspond to points of simple molecular composition, which would not be the case if the components had reacted together to split off water. Furthermore, the complete solidification of a solution at a maximum point at constant temperature indicates that no water is present.

It was found that the exact point of fusion of a mixture could be most readily determined as follows: Solidification was induced, and the whole

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[1] Sulfonation is a slow process, even at high temperatures. Hence, at the freezing point of the mixture, its progress during the course of the experiments was generally negligible entirely. In a few systems, however, it was observed that the temperature of fusion of a mixture changed gradually with the time, pointing to slow sulfonation of the substance under investigation.

[2] This point is discussed more fully in a later section of the paper.

apparatus was placed in a water or paraffin bath, the temperature of which was slightly above the required freezing point, as found by a previous approximate determination. Stirring was constantly maintained in the solution, and the thermometer immersed in this indicated a gradual rise of temperature so long as solid phase was present and absorbing heat by fusion. Disappearance of solid phase was marked by a "hang" in the temperature, succeeded by a rapid rise. At the same time the solution became clear.

By this method freezing points could be obtained, in favorable cases, accurate to within 0.2–0.5°; in some systems, however, the temperatures given are correct only to the nearest degree. The difficulties of observation were especially great on the sulfuric acid side. Points in this region (solid phase H_2SO_4) are of no particular importance. Consequently, after the first series of experiments with the aromatic acids had been completed, the examination of this portion of the systems was omitted, except in special cases. The curve was started from the other end and carried along as far as possible, by successive additions of sulfuric acid, until the composition of the mixture was such that no further compounds were to be expected.

The results of the investigation are collected in the tables below, which are arranged as in the preceding papers of this series. (T = temperature of incipient solidification.) Some typical freezing point curves are shown in the accompanying diagrams.

Aromatic and Aliphatic Acids.

1. *Benzoic Acid.*—The compound $C_6H_5.COOH,H_2SO_4$ was obtained, stable at its maximum, m. p. 87.5°. The freezing point curve is given in Fig. I.

(a) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100.0	98.0	92.1	83.9	69.1	67.4
T	121.8	120.6	115.8	109.6	92.5	90.0

(b) Solid phase, $C_6H_5.COOH,H_2SO_4$.

% $C_6H_5.COOH$	60.2	56.9	51.8	49.5	44.3	39.2	34.2	30.8
T	82.3	84.2	86.2	87.3	86.3	83.2	77.2	72.3
% $C_6H_5.COOH$	26.2	24.2	22.6	18.6				
T	61.4	53.2	44.6	25.8				

(c) Solid phase, H_2SO_4.

% $C_6H_5.COOH$	9.9	8.0	5.7	3.2	0.0
T	—6.2	—1.2	3.2	7.0	10.3

2. *o-Toluic Acid.*—The compound $C_7H_7.COOH,H_2SO_4$ was obtained, stable at its maximum, m. p. 59° (see Fig. III).

(a) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	88.7	78.0	68.1	66.7	61.1	58.1
	102.9	97.8	92.0	83.6	82.2	74.2	67.0

(b) Solid phase, C_7H_7COOH, H_2SO_4

% C_7H_7 COOH	51 9	51 6	47 4	44 3	39 5	37 0	33 6
T	58 7	58 7	58 2	57 6	56 3	54 6	49 1
% C_7H_7 COOH	30 7	25 6	20 1				
T	45 6	33 5	12 0				

(c) Solid phase H_2SO_4

| % C_7H_7 COOH | 4 6 | 2 4 | 0 0 |
| T | 3 0 | 7 2 | 10 3 |

3 *m-Toluic Acid* —In this system two compounds were isolated $2C_7H_7$ COOH,-H_2SO_4 (m p 79 5° by extrapolation) and C_7H_7 COOH H_2SO_4 (m p 63 5°, by extrapolation) Both compounds are unstable at their maxima, but their points of fusion may be readily obtained by a slight extension of the curves, as will be seen from the diagram (Fig I)

(a) Solid phase C_7H_7 COOH

| % C_7H_7 COOH | 100 0 | 84 5 | 74 3 | 67 7 | 64 1 | 61 8 |
| T | 110 0 | 100 5 | 92 0 | 83 6 | 78 7 | 74 9 |

(b) Solid phase $2C_7H_7$ COOH, H_2SO_4

% C_7H_7 COOH	64 7	61 8	60 2	59 5	58 7	55 6	54 1	50 9
T	79 3	78 9	78 3	78 3	78 0	76 2	75 9	72 2
% C_7H_7 COOH	49 9	47 1	45 0	36 3				
T	71 6	68 8	62 3	36 2				

(c) Solid phase C_7H_7 COOH H_2SO_4

| % C_7H_7 COOH | 42 5 | 39 7 | 36 4 | 34 8 | 34 0 | 30 8 | 27 1 | 22 4 |
| T | 61 8 | 58 4 | 55 6 | 54 0 | 52 7 | 46 5 | 37 5 | 20 8 |

(d) Solid phase, H_2SO_4

| % C_7H_7 COOH | 7 7 | 2 4 | 0 0 |
| T | —1 8 | 7 3 | 10 3 |

4 *p-Toluic Acid* —The compound C_7H_7 COOH H_2SO_4 was obtained, unstable at its maximum (m p 100° by extrapolation) The freezing point curve is shown in Fig I

(a) Solid phase, C_7H_7 COOH

| % C_7H_7 COOH | 100 0 | 84 2 | 71 0 | 62 9 | 59 6 | 55 2 | 51 3 | 49 6 | 46 8 |
| T | 180 2 | 167 5 | 154 7 | 143 7 | 137 5 | 127 0 | 116 0 | 111 2 | 100 2 |

(b) Solid phase, C_7H_7 COOH, H_2SO_4

| % C_7H_7 COOH | 45 5 | 42 2 | 37 1 | 32 8 | 28 1 | 23 0 | 21 2 | 16 8 | 14 7 |
| T | 99 5 | 98 9 | 94 9 | 88 5 | 77 5 | 58 7 | 53 0 | 18 0 | 7 5 |

(c) Solid phase, H_2SO_4

| % C_7H_7 COOH | 6 2 | 3 2 | 1 7 | 0 0 |
| T | —2 2 | 3 0 | 5 8 | 10 3 |

5 *α-Toluic Acid* —The compound C_7H_7 COOH, H_2SO_4 was obtained, stable at its maximum, m p 62°

(a) Solid phase, C_7H_7 COOH

| % C_7H_7 COOH | 100 0 | 91 1 | 83 8 | 71 6 | 69 9 | 68 7 | 67 1 | 65 3 | 61 6 |
| T | 76 8 | 71 5 | 67 7 | 59 4 | 56 8 | 55 0 | 53 3 | 50 1 | 40 6 |

(b) Solid phase C_7H_7 COOH, H_2SO_4

| % C_7H_7 COOH | 56 3 | 53 7 | 49 8 | 45 1 | 42 6 | 39 5 | 37 9 | 36 2 | 28 7 | 16 3 |
| T | 58 4 | 69 0 | 61 7 | 62 7 | 60 7 | 60 0 | 58 7 | 55 0 | 47 7 | 15 8 |

(c) Solid phase, H_2SO_4.

% $C_7H_7.COOH$...	6.8	5.1	2.5	0.0
T..............	—20	—3 o	5.6	10.3

6. *Salicylic Acid.*—When sulfuric acid was added to this substance and the temperature raised to melt the solid, water was given off. This evidence of a condensation reaction rendered further work on the system useless
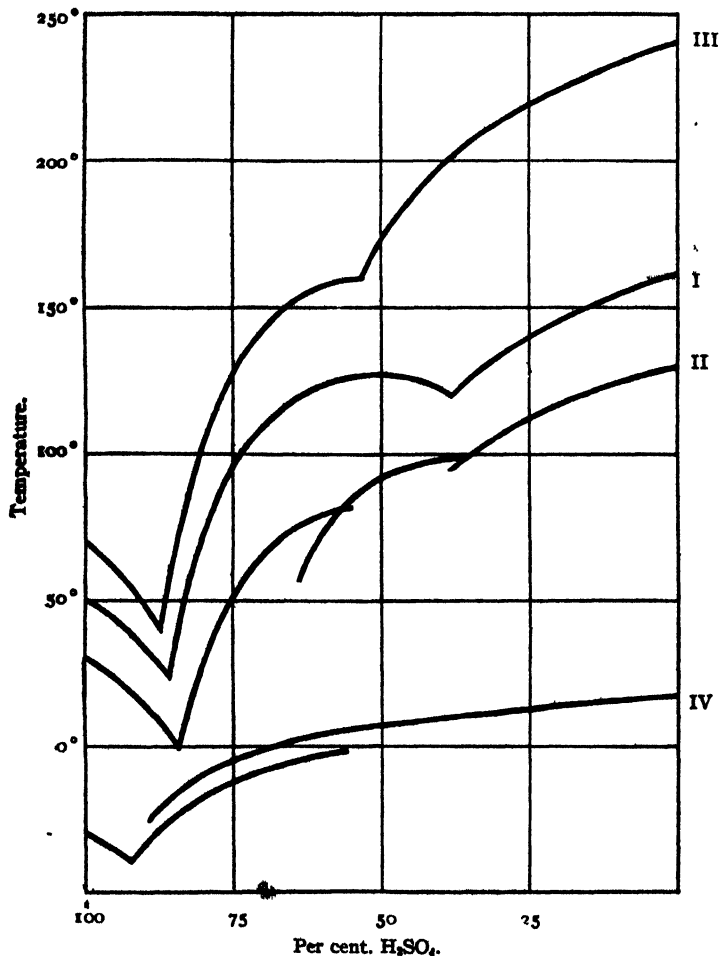
I. Benzoic acid.   Subtract 40° from temperature scale.
II. *m*-Toluic acid.   Subtract 20° from temperature scale.
III. *p*-Toluic acid.   Subtract 60° from temperature scale.
IV. Trichloroacetic acid.   Add 40° to temperature scale.

Fig. I.

7. *o-Nitrobenzoic Acid.*—On an attempt to melt the mixture of acids in this case, a violent reaction took place, leaving nothing in the tube but a charred mass.

8. *Cinnamic Acid.*—This acid also charred with sulfuric acid when the temperature was raised, and no investigation of the system could be made. Hoogewerff and van Dorp[1] record the existence of two addition compounds with the formulas $C_9H_7.COOH,-H_2SO_4$ and $2C_9H_7.COOH,3H_2SO_4$, respectively.

9. *Mandelic Acid.*—Here again the mixture of the two acids darkened on heating and no satisfactory examination of the system could be carried out.

10. *Chloroacetic Acid.*—No compound formation in this system was indicated.

(a) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$	100.0	94.4	88 1	78.9	65.1	62.3	59.7	53.7	46.0
T	61.7	60.5	57.8	52.7	41.1	38.1	34.5	25.2	,9.2

11. *Trichloroacetic Acid.*—The freezing point curve of this system is given in Fig. I It will be seen that the depression of the freezing point of trichloroacetic acid by sulfuric acid is abnormally small. No compound was isolated, but in the region between 11% and 44% trichloroacetic acid the points obtained fall on two regular curves running parallel throughout. It is evident that the lower curve corresponds to an unstable crystalline modification of trichloroacetic acid, with a melting point of approximately 50°.

(a) Solid phase, $CCl_3.COOH$ (I).

% $CCl_3.COOH$...	100.0	89.3	78.1	68.2	58 3	54.0	49.5	41.7	37.7
T.	57.3	56.1	53.4	51.2	49.2	47.9	47 0	44.8	^2.6
% $CCl_3.COOH$...	33.2	30.8	26.1	24 9	21 0	17.9	14.1	11.3	
T	41.9	39.2	39.5	35.3	31.7	29.0	21.6	15.5	

(a) Solid phase, $CCl_3.COOH$ (II).

% $CCl_3.COOH$...	43.9	32.9	21.9	17.8	13.4	7.8
T	38.4	33.8	24.0	20.2	13.4	1.0

(b) Solid phase, H_2SO_4.

% $CCl_3.COOH$...	2.9	0.0
T	7.5	10.3

12. *Crotonic Acid.*—This acid gave with sulfuric acid the equimolecular addition compound $C_3H_5.COOH,H_2SO_4$, stable at its maximum, m. p. 24.5°.

(a) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$...	100.0	93.8	83.5	74.6	69.1	65.9	59.3
T	71.0	67.5	61.9	54.7	47.0	40.4	22.3

(b) Solid phase, $C_3H_5.COOH,H_2SO_4$.

% $C_3H_5.COOH$...	54.9	49.7	43.5	38.1	33.7
T	21.3	24.3	23.3	15.8	1.5

13. *α-Chlorocrotonic Acid.*—Here no addition compounds are indicated by the freezing point curve.

(a) Solid phase, $C_3H_4Cl.COOH$.

% $C_3H_4Cl.COOH$.	100.0	90.4	80.2	69.4	63.5	56 6	52.8
T	99.0	93.5	86.5	79 5	73.2	64.0	58.5
% $C_3H_4Cl.COOH$.	48.1	43.9	39.0	31.0			
T	49.5	41.0	30.0	2.0			

14. *Glutaric Acid.*—Hoogewerff and van Dorp[2] isolated addition compounds of

[1] Hoogewerff and van Dorp, *Rev. trav. chim. Pays-Bas*, 18, 213 (1899).
[2] *Loc. cit.*

sulfuric acid with the following dibasic aliphatic acids: succinic, fumaric, mesaconic. These proved unsuitable for use in the present investigation owing to their high points of fusion, and glutaric acid, which possesses the lowest melting point of the series of saturated dibasic acids, was chosen for examination. An equimolecular addition compound was obtained, stable at its maximum, m. p. 45.5°.

(a) Solid phase, $C_3H_6(COOH)_2$.

% $C_3H_6(COOH)_2$.	100.0	87.4	78.8	70.9	65.2	59.6	54.1	49.0	47.8
T.	95.8	92.9	88.6	82.5	75.7	63.9	51.7	37.1	35.0

(b) Solid phase, $C_3H_6(COOH)_2, H_2SO_4$.

% $C_3H_6(COOH)_2$.	45.5	41.6	39.0	33.5
T.	49.7	47.7	46.0	40.1

Consideration of Results with Acids.

Fourteen acids have been investigated with sulfuric acid. Four of these suffered decomposition on heating, three gave no addition compounds, and seven yielded positive results. Of the eight compounds isolated, seven were of the type $R.COOH, H_2SO_4$, and one of the type $2R.COOH, H_2SO_4$. All compounds were colorless.

An examination of the results shows that the rule enunciated in a previous communication,[1] that the tendency towards addition-compound formation (for acids in pairs) is dependent upon the difference in acidic strengths, holds throughout the entire series. Very weak organic acids readily form addition compounds with a strong acid, such as sulfuric acid. An increase in the acidic strengths of the organic acid is accompanied by the loss of this property. This is illustrated in the following table where the results of the present investigation and those obtained by Hoogewerff and van Dorp[2] are collected. The dissociation constants are those given by Ostwald.[3]

Acids forming addition compounds.		Acids not forming addition compounds.	
Acid.	100 K.	Acid.	100 K.
Benzoic.	0.0060	o-Chlorobenzoic.	0.132
o-Toluic.	0.0120	m-Chlorobenzoic(?)	0.0155
m-Toluic (2 compounds)	0.00514	p-Chlorobenzoic(?)	0.0093
p-Toluic.	0.00515	o-Bromobenzoic.	0.145
a-Toluic.	0.00556		
m-Bromobenzoic.	0.0137		
Cinnamic (2 compounds)	0.00355		
Crotonic.	0.00204	Chloroacetic.	0.155
Succinic.	0.00665	Trichloroacetic.	121.0
Glutaric.	0.00475	a-Chlorocrotonic.	0.072
Fumaric.	0.093		
Mesaconic.	0.0790		

[1] Kendall, *Loc. cit.*

[2] Hoogewerff and van Dorp, *Loc. cit.* It must be remembered that negative results obtained by Hoogewerff and van Dorp do not disprove the existence of addition products, since the mixtures investigated by them may not have had compositions suitable for the isolation of compounds.

[3] Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

The results of the above table agree with those obtained previously[1] in indicating that addition compounds of the type acid–acid are, in fact, *oxonium salts*, the acidic properties of the weaker acid being suppressed by the stronger, and basic (unsaturated) properties being induced in the carbonyl group.   Under this view the formulas of the compounds obtained are:

$$ \underset{\underset{OH}{|}}{R-C}=O \diagdown_{O-(SO_2).OH}^{H} \qquad \text{and} \qquad \underset{\underset{OH}{|}}{R-C}=O \diagdown_{O-(SO_2)-O}^{H} \diagup^{H} O=\underset{\underset{OH}{|}}{C}-R $$
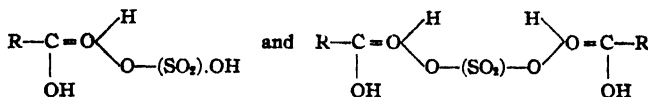
In the former, sulfuric acid acts as a monobasic acid; in the latter, as a dibasic acid.

Phenols.

15. Phenol.—The compound $2C_6H_5OH,H_2SO_4$ was obtained, stable at its maximum, m. p. 15.5° (see Fig. III).

(a) Solid phase, $C_6H_5.OH$.

% $C_6H_5.OH$	100.0	94.1	86.6	79.4	72.0
T	42.4	35.5	30.5	23.4	13.4

(b) Solid phase, $2C_6H_5.OH,H_2SO_4$.

% $C_6H_5.OH$	66.8	61.3	55.4	51.8	49.5	45.7	42.7	39.5
T	15.0	16.0	12.2	10.4	8.0	6.0	2.5	—2.(
% $C_6H_5.OH$	36.3	34.1						
T	—7.0	—10.0						

16. o-Cresol.—In this system no addition compounds could be isolated, supercooling making a satisfactory investigation very difficult.

(a) Solid phase, $C_7H_7.OH$.

% $C_7H_7.OH$	100.0	89.1	76.8	68.7	66.2	61.9
T	30.4	26.2	18.8	9.6	6.2	1.0

17. p-Cresol.—Here two compounds were isolated, both stable at their points of fusion; $2C_7H_7OH,H_2SO_4$ (m. p. 11.0°) and $C_7H_7.OH,2H_2SO_4$ (m. p. 93.5°).   The flatness of the maximum in the case of the former compound indicates that it is largely dissociated into its components on fusion, but the form of the curve for the second addition product, together with its surprisingly high melting point, makes it evident that the compound is very stable.   The freezing point curve is given in Fig. II.

(a) Solid phase, $C_7H_7.OH$.

% $C_7H_7.OH$	100.0	90.4	82.2	75.4
T	34.6	29.4	22.1	11.6

(b) Solid phase, $2C_7H_7.OH,H_2SO_4$.

% $C_7H_7.OH$	68.0	62.6	58.5	54.1	50.5	45.4
T	11.0	11.0	9.3	7.5	5.0	9.0

(c) Solid phase, $C_7H_7.OH,2H_2SO_4$.

% $C_7H_7.OH$	56.0	48.7	39.5	34.7	33.8	28.6	21.6	16.2	12.5
T	24.0	57.3	84.1	91.9	93.4	90.9	78.2	57.8	40.2

18. o-Xylenol.—In this system two compounds were also isolated, analogous to those obtained in the case of *p*-cresol.   The compounds $2C_8H_9OH,H_2SO_4$ (m. p. 70°)

[1] Kendall, THIS JOURNAL, 36, 1722 (1914).

and $C_6H_5.OH,H_2SO_4$ (m. p. 90°) were obtained. Both are stable at their melting points (see Fig. II).

(a) Solid phase, $C_6H_5.OH$.

% $C_6H_5.OH$......	100.0	87.5	80.2	75.8	72.1	63.7
T...............	63.7	57.6	50.3	47.0	42.4	31.6
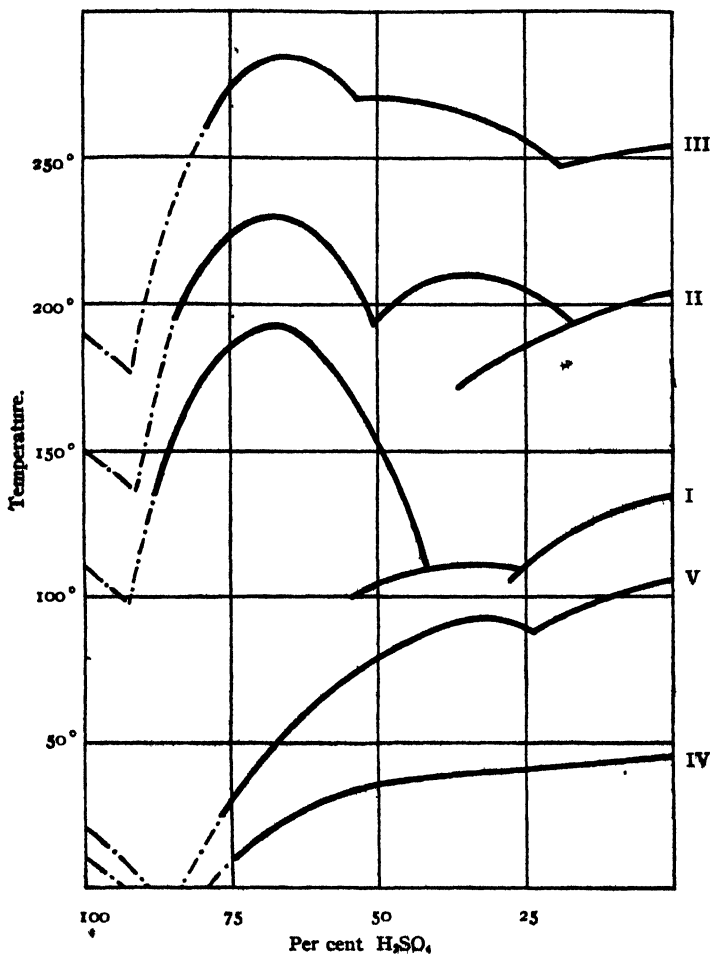
I. *p*-Cresol.   Subtract 100° from temperature scale

II   *o*-Xylenol.   Subtract 140° from temperature scale.

III   *p*-Xylenol.   Subtract 180° from temperature scale.

IV   *p*-Nitrophenol.   Temperature scale correct

V   *m*-Nitrophenol.   Subtract 10° from temperature scale.

Fig II

(b) Solid phase, $2C_6H_5OH,H_2SO_4$

% C_6H_5OH	70 9	66 9	60 2	54 4
T	68 0	70 0	68 9	63 4

(c) Solid phase, $C_6H_5OH\ H_2SO_4$

% C_6H_5OH	50 7	47 8	44 6	41 5	34 0	30 4	25 3	20 3	16 1
T	53 8	60 8	71 5	80 7	90 0	89 4	84 8	72 8	58 3

19 p-Xylenol —Two addition compounds were obtained in this system, the equimolecular compound C_8H_9OH,H_2SO_4 (m p 91°) and the compound $C_8H_9OH,2H_2SO_4$ (m p 104°) Both are stable at their maxima (see Fig II)

(a) Solid phase C_8H_9OH

% C_8H_9OH	100 0	91 1	81 1
T	74 0	71 0	67 9

(b) Solid phase, C_8H_9OH,H_2SO_4

% C_8H_9OH	71 7	67 0	61 7	54 0
T	80 6	84 2	87 2	90 4

(c) Solid phase $C_8H_9OH\ 2H_2SO_4$

% C_8H_9OH	46 4	40 1	32 8	24 7
T	92 4	101 0	104 0	91 9

20 Thymol —On first addition of sulfuric acid to thymol the point of fusion was lowered, as in normal cases   After about 20% of acid had been added, however, two immiscible layers formed and the point of fusion (in the layer richer in thymol) remained practically constant on further addition of acid   An attempt to cause complete admixture of the two liquids (at the point 53% thymol) by raising the temperature resulted in sulfonation taking place, a white solid separating out   This did not melt at 100°, at which temperature water was given off   The system was not examined further

(a) Solid phase $C_{10}H_{13}OH$

% $C_{10}H_{13}OH$	100 0	92 4	83 3	72 2	64 7	52 7
T	49 6	47 1	43 0*	1 0*	42 0*	?

21 o-Nitrophenol —No addition compound was here isolated   The form of the curve indicates also that none is present in solution, the freezing point depression being extremely small (see Fig II)   o Nitrophenol here behaves quite differently from its isomers, m-nitrophenol and p nitrophenol   Both of these form addition compounds, as will be seen in Tables XXII and XXIII below   Similarly o-nitrophenol does not yield addition products with aniline[1] or with dimethylpyrone,[2] while the other nitrophenols give compounds in both cases   This anomalous behavior of o-nitrophenol is evidently connected in some way with stearic hindrance, since in acidic strength it lies between the other two[3] and should give exactly similar results

(a) Solid phase, $C_6H_4NO_2OH$.

% $C_6H_4NO_2OH$	100 0	93 6	88 0	82 3	75 7	74 4	68 9	67 9
T	45 0	43 9	42 4	41 5	40 7	41 4	39 5	40 6
% $C_6H_4NO_2OH$	66 5	63 8	59 3	52 6	45 6	40 7	32 0	25 8
T	39 1	38 7	39 3	37 0	33 5	30 0	21 0	11 0

[1] Kreeman and Rodinis, *Monats*, 27, 136 (1906).
[2] Kendall, THIS JOURNAL 36, 1237 (1914).
[3] Holleman, *Rec trav chim Pays-Bas*, 21, 444 (1902).

22. *m-Nitrophenol.*—One compound was obtained, $2C_6H_4.NO_2.OH,H_2SO_4$, (m. p. 83°), stable at its maximum (see Fig. 2).

(a) Solid phase, $C_6H_4.NO_2.OH$.

% $C_6H_4.NO_2.OH$	100.0	93.3	87.7	82.0					
T	95.4	92.5	89.4	84.7					

(b) Solid phase, $2C_6H_4.NO_2.OH,H_2SO_4$.

% $C_6H_4.NO_2.OH$	73.5	68.5	60.5	55.2	51.4	45.9	37.7	31.7	24.7
T	81.7	82.7	78.6	73.5	69.4	62.3	52.2	39.4	18.0

23. *p-Nitrophenol.*—Here also one compound was obtained, $2C_6H_4.NO_2,H_2SO_4$, (m. p. 90°), stable at its maximum.

(a) Solid phase, $C_6H_4.NO_2.OH$.

% $C_6H_4.NO_2.OH$	100 0	92.7	83.9	76.9			
T	113.8	109.4	102.7	97 0			

(b) Solid phase, $2C_6H_4 NO_2.OH,H_2SO_4$.

% $C_6H_4.NO_2.OH$	68.1	64.1	58.4	53.0	50 6	44 7	35.6
T	89 9	88.3	80 7	73.5	70.4	60 3	35 1

Consideration of the Results with Phenols.

Nine phenols have been investigated with sulfuric acid. One of them suffered sulfonation, two gave negative results, the remaining six yielded addition compounds. Of the nine compounds isolated, five were of the type $2R.OH,H_2SO_4$, one of the type $R.OH,H_2SO_4$, and three of the type $R.OH,2H_2SO_4$.

The addition of sulfuric acid to a phenol is accompanied in general by a darkening in color, the mixture becoming red and in some cases almost black. Only in one system, *p*-cresol, were the solutions light-colored throughout. In the solid form, however, the addition products were colorless, or at most, only faintly tinted. This darkening, coupled with the viscous nature of the mixture, made the investigation of the systems extremely difficult. Supercooling occurred, in almost all systems, to a considerable extent; so that in some cases a compound (*e. g.*, the compound $2C_8H_9.OH,H_2SO_4$, in the case of *p*-xylenol) was entirely missed on the first examination, and only on a repetition of the experiment found to exist. It is extremely probable, consequently, that in certain systems some of the addition products present in solution were not isolated.

With regard to the structural formula of the compounds obtained, it is rather difficult to decide. The analogy between the addition products here described and those obtained in the case of organic acids renders the same oxonium structure extremely probable. The generally accepted view[1] for the representation of compounds of the type phenol-acid assumes that the phenol first goes over to the tautomeric ketonic form, *e. g.*,

[1] Gomberg and Cone, *Ann.*, **376**, 220 (1910).
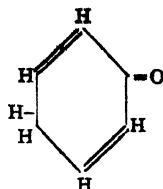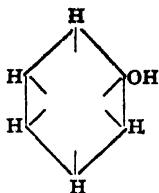
On this assumption, addition takes place on the carbonyl group, as in the case of acids.   But it is also possible for the reaction to be explained directly, by assuming addition on the —OH group, as in the case of alcohols.[1]

According to either of the above hypotheses, it is easy to represent compounds of the types $R.OH,H_2SO_4$ and $2R.OH,H_2SO_4$.   In the former sulfuric acid acts as a monobasic acid, in the latter as a dibasic acid.   The third type of compound, however, $R.OH,2H_2SO_4$, presents some difficulties, since it is impossible to express it, under the scheme followed throughout this series of papers, except by the assumption of hexavalent oxygen.
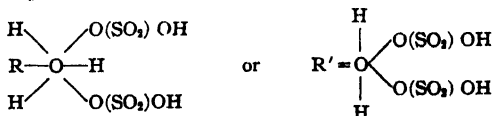
This assumption has previously been made by McIntosh[2] to explain the compounds obtained with dimethylpyrone and the halogen acids.   It is, of course, supported by the hexavalency of sulfur.

While the structural formula of the compounds phenol-acid cannot be definitely fixed, it may be pointed out here that it is impossible to represent compounds of the third type under the hypothesis that these products are carbonium salts.[3]   According to this theory an equimolecular addition compound is considered to be formed as follows:
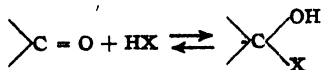
addition taking place through the breaking up of the double bond of the carbonyl linkage.   It is obvious, however, that a compound of the formula $R.OH,2H_2SO_4$ cannot be represented according to this view, and an oxonium structure must be admitted.

The investigation of systems of the type phenol-acid is at present being continued.

Aldehydes, Ketones and Anhydrides.

24. *p-Oxybenzaldehyde.*—On addition of sulfuric acid to this substance, a dark red

[1] Maass and McIntosh, THIS JOURNAL, 30, 1284 (1912).

[2] McIntosh, *Ibid.*, 32, 542 (1910).

[3] Gomberg and Cone, *Ann.*, 376, 220 (1910).

coloration was produced. When the temperature was raised, charring occurred, and the investigation of the system could not be continued.

25. *p-Nitrobenzaldehyde.*—No addition compound was isolated.

(a) Solid phase, $C_6H_4.NO_2.CHO$.

% $C_6H_4.NO_2.CHO$	100.0	90.6	79.7	73.2	65.0	55.4	49.7	49.5
T	104.4	100.7	94.8	90.9	85.0	76.6	74.5	74.8
% $C_6H_4.NO_2.CHO$	47.3	44.6	43.9	41.1	40.2	34.5	33.7	24.1
T	73.0	70.4	70.4	67.1	66.7	54.0	56.5	32.6

26. *Vanillin.*—When sulfuric acid was added, the mixture became dark-colored and decomposition began to occur, so that no examination of the system could be made. Hoogewerff and van Dorp[1] record the isolation of an equimolecular compound.

27. *Piperonal.*—Here again darkening of the mixture prevented any examination of the system. Hoogewerff and van Dorp, however, record having isolated the following compound: $2C_6H_3(O_2CH_2).COH,3H_2SO_4$.

28. *Acetophenone.*—The compound $2CH_3.CO.C_6H_5,H_2SO_4$ was obtained, stable at its maximum (m. p. 29°). The system could not be completely investigated owing to the fact that the solutions became dark and viscous.

(a) Solid phase, $CH_3.CO.C_6H_5$.

% $CH_3.CO.C_6H_5$	100.0	95.8	95.2	89.0
T	18.7	17.2	17.4	13 9

(b) Solid phase, $2CH_3.CO.C_6H_5,H_2SO_4$.

% $CH_3.CO.C_6H_5$	86.3	80.8	69.0	68.9	68.6	63.0	59.9	54.9	51.1
T	17.6	23.8	28.4	28.7	29.9	28.0	25.0	22.5	18.5

29. *Benzophenone.*—The compound $C_6H_5.CO.C_6H_5,H_2SO_4$ was obtained, stable at its maximum (m. p. 64° (see Fig. III)).

(a) Solid phase, $C_6H_5.CO.C_6H_5$.

% $C_6H_5.CO.C_6H_5$	100.0	96.4	92.9	88.7	79.8	70.9
T	47.8	46.4	44.5	42.1	38.0	26.5

(b) Solid phase, $C_6H_5.CO.C_6H_5,H_2SO_4$.

% $C_6H_5.CO.C_6H_5$	64.5	54.1	46.2	42.6	38.8	35.7	32.6	29.6
T	56.6	63.0	63.9	61.9	59.4	55.2	48.7	39.1

30. *Benzil.*—Darkening of the mixture here made an examination impossible. Hoogewerff and van Dorp record the isolation of an equimolecular compound.

31. *Dimethylpyrone.*—Three compounds of this substance with sulfuric acid were isolated: $2C_7H_8O_2,H_2SO_4$ (m. p. 103.6°), $C_7H_8O_2,H_2SO_4$ (m. p. 96°), and $2C_7H_8O_2,3H_2SO_4$ (m. p. 44.8). The first and third of these are just stable at their maxima. Mixtures containing less than 30% dimethylpyrone supercooled to a solid glassy mass, consequently the system could not be completed. It seems probable from the form of the curve (see Fig. III) that other compounds exist. Dimethylpyrone is a stronger base than any of the other substances investigated in this paper; the addition compounds formed, therefore, are very little dissociated on fusion. The curve recalls strongly that of the system sulfuric acid–water, the latter substance being of approximately the same basic strength as dimethylpyrone.[2]

(a) Solid phase, $C_9H_8O_2$.

% $C_9H_8O_2$	100.0	85.4	76.1	71.5
T	132.0	124.0	115.0	109.0

[1] Hoogewerff and van Dorp, *Loc. cit.*

[2] Walker, *Ber.*, **34,** 4115 (1901).

(b) Solid phase, $2C_9H_8O_2,H_2SO_4$

% $C_9H_8O_2$	66 9	63 5	61 1	57 3	55 5
T	. 103 6	101 8	100 2	90 4	84 2

(c) Solid phase, $C_9H_8O_2,H_2SO_4$

% $C_9H_8O_2$	. 53 0	51 3	50 6	47 1	46 2	43 3	41 8	40 5	40 1
T	88 1	93 4	96 0	93 4	90 9	72 5	56 0	41 6	36 6

(d) Solid phase $2C_9H_8O \cdot H_2SO_4$

% $C_9H_8O_2$	39 5	38 3	36 1	34 1	32 2	30 4
T	44 3	43 1	37 6	29 3	18 2	6 0

32 Benzoic Anhydride —In this system three compounds were obtained $2C_{14}H_{10}O_3,H_2SO_4$ (m p 52 5° by extrapolation) $C_{14}H_{10}O_3 H_2SO_4$ (m p 70 5°) and $C_{14}H_{10}O_3,2H_2SO_4$ (m p 60°) The first of these is unstable at its maximum point, the others are stable   The freezing point curve is given in Fig III

(a) Solid phase $C_{14}H_{10}O_3$

% $C_{14}H_{10}O_3$	100 0	94 8
T	39 5	38 9

(b) Solid phase, $2C_{14}H_{10}O_3 H_2SO_4$

% $C_{14}H_{10}O_3$	90 2	85 7	81 0	77 2	73 5
T	42 3	45 3	49 2	50 0	51 0

(c) Solid phase, $C_{14}H_{10}O_3 H_2SO_4$

% $C_{14}H_{10}O_3$	67 6	62 2	55 4	49 7	43 7	37 8	37 4
T	57 3	64 3	69 4	70 2	67 6	59 1	58 3

(d) Solid phase, $C_{14}H_{10}O_3,2H_2SO_4$

% $C_{14}H_{10}O_3$	36 1	31 5	26 5	15 8
T	58 7	58 7	55 4	25 0

33 Succinic Anhydride —The study of this system proved unsatisfactory, as the anhydride sublimes extremely readily at high temperatures   No conclusive results were obtained

34 Phthalic Anhydride —This system also gave no definite results

35 Coumarin —The compound $C_9H_6O_2 H_2SO_4$ was obtained stable at its maximum, (m p 35 5°)

(a) Solid phase $C_9H_6O_2$

% $C_9H_6O_2$	100 0	89 2	80 7	73 1	68 3	63 5	58 4
T	68 4	62 3	53 4	51 8	46 5	40 4	30 8

(b) Solid phase $C_9H_6O_2,H_2SO_4$

% $C_9H_6O_2$	54 2	50 5	46 2	42 6	38 4	35 2
T	32 7	35 5	34 5	32 3	24 0	14 0

Consideration of Results with Aldehydes, Ketones and Anhydrides.

From the twelve systems investigated, nine addition compounds were isolated   The four aldehydes examined gave no definite results, yet it must not be assumed from this that aldehydes do not react with sulfuric acid to form addition compounds, for with diluted acid Hoogewerff and van Dorp obtained compounds in the cases of piperonal and vanillin   The fact is that, in most cases, the reaction is so violent that the process is carried past the addition stage   Aldehydes, in general, exhibit a greater

tendency than ketones to form addition products with acids, as will be shown in a subsequent paper dealing more fully with these two classes of substances.

The four ketones here investigated gave five addition products.   Aceto-
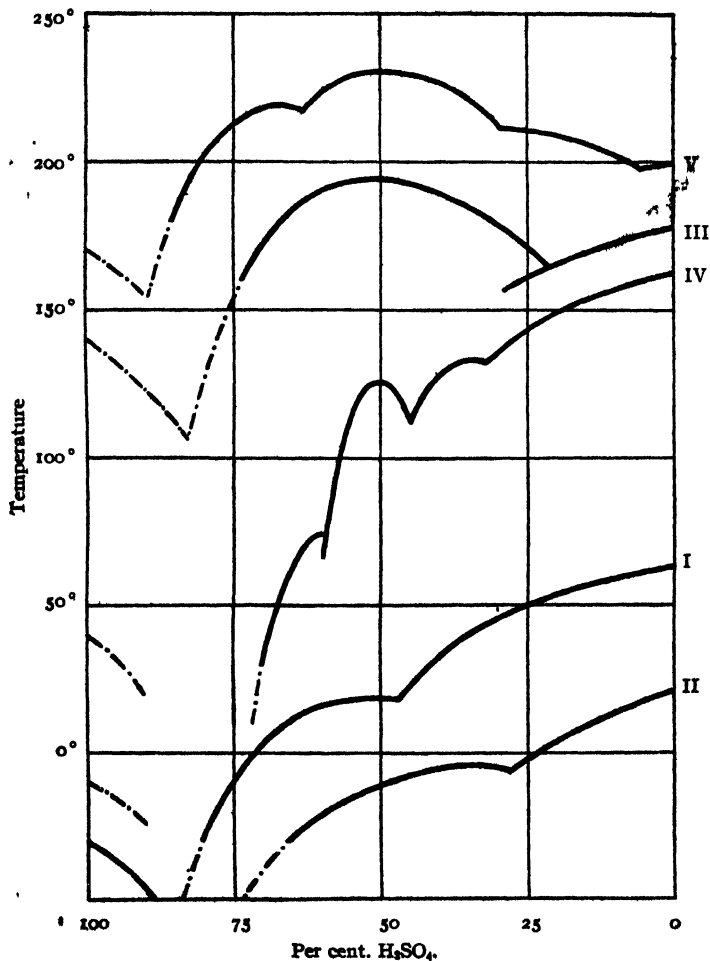
I. o-Toluic acid.   Add 40° to temperature scale.
II. Phenol.   Add 20° to temperature scale.
III. Benzophenone.   Subtract 130° from temperature scale.
IV. Dimethylpyrone.   Subtract 30° from temperature scale.
V. Benzoic anhydride.   Subtract 160° from temperature scale.

Fig. III.

phenone and benzophenone yielded compounds of the types $2R.CO.R',$-H_2SO_4 and $R.CO.R,H_2SO_4$, respectively. In the former, sulfuric acid acts as a dibasic acid, in the latter as a monobasic acid. Dimethyl-pyrone gave compounds of both these types, and also the addition product $2C_7H_8O_2,3H_2SO_4$. Compounds of this type have previously been obtained with dimethylpyrone and other acids.[1]

The four anhydrides investigated gave four addition products. Two of these were equimolecular, the others were of the formulas $2C_{14}H_{10}O_3$, H_2SO_4 and $C_{14}H_{10}O_3,2H_2SO_4$, respectively. In a substance such as benzoic anhydride the possibilities for addition compound formation are so numerous that no structural representation of the products isolated is attempted.

General Conclusions.

Thirty-five organic substances in all have been investigated with sulfuric acid, and twenty-six addition compounds have been obtained. These include:

9 compounds of the type A_2B (A = organic substance, B = sulfuric acid).

12 compounds of the type AB (or A_2B_2).

1 compound of the type A_2B_3.

4 compounds of the type AB_2 (or A_2B_4).

It is thus seen that the compounds form a regular series in four steps. These compounds have been explained on the assumption of oxonium salt formation developed in previous papers.[2] The quantitative results, where available, are in complete accordance with this view.

The reasons for asserting definitely that these compounds are addition and not sulfonation products—a point already briefly referred to in the introduction—may here be discussed more fully. The freezing point curves shown above offer in themselves sufficient evidence in proof of this important point, since all maxima appear at points of simple molecular composition. This could occur only by chance if the reaction in-

[1] Kendall, *Loc. cit.*

[2] Kendall, *Loc. cit.* The substances examined all contain oxygen; in cases where this element is absent (*e. g.*, aromatic hydrocarbons) a new explanation must be sought. In the first place, the addition might take place by means of the unsatisfied carbon valences of the benzene ring. This is supported by the fact that the saturated aliphatic hydrocarbons do not form sulfonation products. On the other hand, no evidence has been obtained throughout the present series of investigations of any difference in behavior between aliphatic and aromatic substances which would indicate activity of such a nature. An alternative hypothesis (first suggested to us by Dr. J. M. Nelson) is that the carbon atom is potentially hexavalent, just as the oxygen atom is potentially quadrivalent. The addition process would thus be essentially similar in its nature to that investigated in this paper, the basic properties of carbon, however, probably being found much weaker than those of oxygen. It is hoped to investigate this point after the study of the different classes of oxonium compounds has been completed.

volved were sulfonation and not addition, and that such a chance could
happen twenty-six times without a single exception is a manifest impossi-
bility. Furthermore, sulfonation takes place with splitting-off of water,
and in no case (except those expressly mentioned above) was evolution
of water observed. The fact that complete solidification at constant tem-
perature occurs at a maximum point is decisive proof that a pure sub-
stance is under examination and it is very improbable[1] that this pure
substance can be other than an addition product.

Another fact is extremely important in this connection. Sulfonation
is, even at high temperatures, a slow reaction, while all products isolated
in this paper are formed immediately. For instance, a basic substance
such as aniline must be heated with sulfuric acid to 180–190° for *four or
five hours* before sulfonation is complete.[2] On the other hand, when *p*-cresol
and sulfuric acid (in the molecular proportions of one to two) are warmed
together to 35° to melt all *p*-cresol, and the mixture rapidly cooled in an
ice-salt mixture, with vigorous stirring, complete solidification occurs
at once. A white crystalline mass is produced, which melts at 93 5°;
and is evidently a pure compound. The reaction is here, so far as can be
judged, *instantaneous*, even at the low temperature employed.

This is again in agreement with the theory that the reaction is an oxon-
ium salt formation and ionic in its nature.[3] The basic organic substance,
in accordance with its unsaturated nature, is the ionizing medium, and
an addition compound (for example, equimolecular) is formed thus:

$$\diagup C = O^+ + H^+ + HSO_4^- \;\rightleftarrows\; \diagup C = O\diagup\!\!\!\diagdown {}^{O(SO_3)OH}_{H}.$$
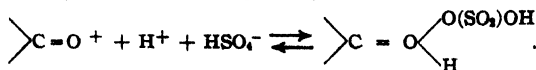
The reaction represented in the above equation is to be regarded either
as the first step in the sulfonation process, or as a parallel reaction consid-
erably faster than the one leading to the more stable sulfonic acids.[4] In
the former case the completion of the process involves a rearrangement
of the molecule and the splitting off of water. Under the latter view,
dissociation of the addition compound into the original constituents
would take place before sulfonation. The reactions that occur would thus
be comparable with those involved in the formation of acetamide by heat-
ing ammonium acetate.

The results of the investigation may be summarized in the statement
that sulfonation is preceded by the formation of addition compounds,

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[1] If sulfonation had taken place a sulfonic acid and water would be present.
Sulfonic acids decompose on fusion and have no definite melting points. The only
possibility for a constant point of fusion, if we assume sulfonation, is that the sulfonic
acid forms a very stable hydrate.

[2] Cohen, *Practical Org. Chem.*, 1904, p. 150.

[3] Kendall, THIS JOURNAL, 36, 1242 (1914).

[4] For the suggestion of this second view we are indebted to Professor Stieglitz.

of the nature of oxonium salts. This reaction is *ionic* and *instantaneous*. The addition compounds obtained are possibly—but not necessarily— real intermediate products in the formation of sulfonic acids.

It will be obvious that similar reactions, such as nitration, may be considered to follow an exactly similar course.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MONTANA]

SOME SALTS OF THE CHLOROACETIC ACIDS.

BY W G BATEMAN AND A B HOEL
Received October 9, 1914

While looking up constants in connection with the regular work in the organic laboratory, we noted the paucity of information in the literature relating to the derivatives of the chloroacetic acids. The work described in this paper was then undertaken to fill up some of the gaps encountered.

$CH_2Cl.CO_2NH_4$.—The difficulty of obtaining neutral ammonium salts of organic acids from water solutions has many times been mentioned. In the case of chloroacetic acid this difficulty is increased by the fact that both ammonium hydroxide and carbonate increase in aqueous solutions the hydrolysis of the acid into glycollic acid and hydrogen chloride. It was decided, therefore, to prepare this salt by passing ammonia into an absolute alcohol solution of the acid. This method is the same as that employed by Keiser and McMaster[1] who prepared many neutral ammonium salts by this method, but whose papers did not come to our notice until this work was practically finished.

Ammonia, made by heating the concentrated hydroxide and dried by passing through a high soda lime tower, was passed into a solution of monochloroacetic acid in absolute alcohol. In a few minutes a heavy, white precipitate fell down which was filtered off, washed with alcohol, in which it was sparingly soluble and dried in a current of air. The product was snow white and beautifully crystalline. It is readily soluble in water, to which at first it imparts a neutral reaction, which, in a few minutes, becomes acid, due to hydrolysis. The salt is also soluble in methyl alcohol, but insoluble in ether, benzene or chloroform.

When heated in an open dish ammonium chloroacetate volatilizes completely without charring, and giving off dense fumes like those of ammonium chloride.

The only mention we find of this salt is in Beilstein[2] who quotes Rival[3] as saying the salt is "unbeständig." Our product seemed quite stable,

[1] *Am. Chem J.*, 49, 84 (1913), THIS JOURNAL, 36, 742 (1914)
[2] *Beilstein, Ergänzb.*, I, 167.
[3] Rival, *Ann.*, 12, 504

no changes being observed, after several months' standing. It is not deliquescent. In a few samples a slight but unmistakable odor like that of impure acetamide was perceived. Chloroacetamide with its unknown odorous companion might here be formed in two ways: by a slight amount of chloroacetic ester being formed and reacting with the ammonia, or by a slight decomposition of the ammonium salt itself.

Calc. for $NH_4CH_2ClCO_2$: N, 12.55; found (by Kjeldahl), 12.51.

$CCl_3CO_2NH_4$.—This salt was prepared like the above, by passing dry ammonia into an absolute alcohol solution of trichloroacetic acid. No precipitate was formed; the solution gave out so much heat that it was cooled in ice water. After passing the gas for some minutes, the solution became very viscous. The addition of ether gave no precipitate, but after standing some days a skim of crystals collected on the top. The alcohol evaporated away very slowly, suggesting the possibility of some combination involving it. At the same time the solution gave off a most agreeable odor which was found to be due to trichloroacetic ester. Upon gentle heating the alcohol was given off slowly, leaving behind a thick, odorless syrup. When this was stirred and briskly beaten it solidified into a mass of slightly moist white crystals, which were dried in a desiccator. The product gave a neutral reaction to water solutions, which quickly became strongly acid. It was soluble in alcohol, ether and ethyl acetate. Careful heating in an open dish caused complete volatilization, without charring, in white fumes having the odor of the acid. Upon stronger heating the compound decomposes, gives off ammonium chloride, irritating vapors of carbonyl chloride and, in addition, carbon monoxide. No mention of this salt was found, but Rival[1] describes the dihydrate and several acid compounds.

Calc. for $NH_4CCl_3CO_2$: N, 7.75; found (by Kjeldahl), 7.63.

$Cu(CH_2ClCO_2)_2.4H_2O$.—This compound was formed by adding a slight excess of copper carbonate to a water and alcohol solution of chloroacetic acid. After filtering, the deep blue solution was set aside to crystallize. Beautiful, deep green crystals formed, less dark in hue than those of copper acetate. These are soluble in strong alcohol, forming a bright green solution.

Calc. for $Cu(CH_2ClCO_2)_2.4H_2O$ Cu, ——; found, 19.71, 19.84; 0.2261 g. heated at 102–105° for some hours lost 0.0495 g.; water calculated for above, 22.30%; found, 21.91%.

$Cu(CH_2ClCO_2)_2$ was prepared by dehydrating the tetrahydrate, the product being a bright blue-green powder. This dissolves in absolute alcohol, not so readily as the hydrate, giving a greenish blue solution. The anhydrous salt is also less soluble in water, with which it forms a slight, white precipitate, probably a basic salt. Some of this compound

[1] *Loc. cit.*

was dissolved in alcohol and dry ammonia passed in. In addition to some of the white ammonium salt, a considerable amount of a deep blue crystalline substance was formed. This was judged to be $Cu(NH_3)_4(CH_2ClCO_2)_2$ by its resemblance to analogous compounds, but the sample was lost during analysis.

Calc. for $Cu(CH_2Cl.CO_2)_2$: Cu, 25.37, found, 25.46.

In an attempt to prepare an addition product of copper chloroacetate and phenylhydrazine, the two were brought together in alcohol. A very vigorous reaction occurred in the cold. Cuprous oxide was precipitated and nitrogen evolved in large quantities. At the same time, a substance having a most agreeable spicy odor was formed. Copper acetate is reduced in hot solutions by hydrazines in a similar fashion,[1] but the halogen substituted salt is much more energetic. We hope to investigate this reaction further.

$Zn(CH_2ClCO_2)_2.2H_2O.$—Prepared in the same way as the preceding. This compound formed in fan shaped clusters of large almost transparent crystals. These were very deliquescent, being wet after standing over concentrated sulfuric acid. During this drying the crystals changed form and appearance, becoming smaller and white. Analysis of the higher hydrate were unsatisfactory, but indicated the tetrahydrate.

Calc for $Zn(CH_2ClCO_2)_2.2H_2O$· Zn, 22 66; found, 23

$Pb(CH_2ClCO_2)_2.$—Prepared by heating together equivalent quantities of pure litharge and the acid in water solution. Upon cooling the solution the salt crystallized out in fine, white, prismatic plates. Both salt and solutions have a sweet taste. The salt is sparingly soluble in cold water, much more soluble in hot.

Calc . Pb, 52.55, found, 52.73.

$Mn(CH_2ClCO_2)_2CH_2ClCO_2H.4H_2O.$—When water solutions of monochloroacetic acid were treated with manganese carbonate, it was found impossible to neutralize the solution. Even when cold some black, hydrated manganese dioxide always formed, the quantity of which was increased by heating. Both hot and cold solutions after filtering and evaporating gave crops of transparent crystals having no, trace of color. Upon drying these became pure white and microcrystalline. Solutions of this were rather strongly acid, and even the moist salt had an acid odor.

Calc.: Mn, 13.46; found, 13.51.

Slightly soluble in cold alcohol and ether. Soluble in acetic ester.

$Mn(CH_2ClCO_2)_2CH_2ClCO_2H.2H_2O.$—When the tetrahydrate was heated for some time below 105° it readily lost two molecules of water, became somewhat more bulky and rather fluffy in appearance. A very little

[1] Tafel, *Ber.*, 25, 413 (1892); Gatterman, Johnson and Bichle, *Ibid.*, 25, 1075 (1892).

acid was given off during the heating and the faintest tinge of pink color was noted.

<div align="center">Calc.: H₂O, 8.81; Mn, 15.51; found, 8.05, 15.32.</div>

<div align="center">Calc.: H_2O, 8.81; Mn, 15.51; found, 8.05, 15.32.</div>

When the dihydrate or tetrahydrate were heated much above 105° water was given off very slowly, but the amount of acid volatilized was much increased. The residue acquired the familiar pink color of normal manganous salts. Neither the anhydrous acid nor the normal salt could be secured in this way, since decomposition occurred on stronger heating with the darkening of the residue due to the formation of manganese dioxide.

When the acid tetrahydrate is dissolved in hot alcohol, there is precipitated, upon cooling, a very bulky white crystalline mass, which is freed from the solvent with considerable difficulty. As the alcohol evaporates away the compound shrinks in bulk, and has the same appearance when dry as the hydrate described above, looking much like purified cellulose. Analysis showed it to be the same compound.

<div align="center">Calc.: Mn, 15.51; found, 15.17.</div>

The compound lost water and acid by prolonged drying or gentle heating.

$Ni(CH_2ClCO_2)_2.3H_2O$.—Obtained by treating water solutions of the acid with nickel carbonate. The deep green solutions upon evaporation gave only thick, green syrups, which did not crystallize upon seeding with a crystal of nickel acetate, or by treating with alcohol or ether. Finally, heated on the water bath, both solutions became very viscous, and, after standing some time in a desiccator, gave apple-green crystals.

<div align="center">Calc.: Ni, 19.61; found, 19.37.</div>

$C_6H_5.NHNH_2(CH_2ClCO_2H)_2$.—Formed by bringing together the proper quantities of phenylhydrazine and acid in absolute alcohol. The compound formed in heavy, white, needle-like crystals, which were filtered, washed with alcohol and dried. They had a faint odor of the hydrazine, which increased on standing showing the salt to be unstable. Soluble in water.

<div align="center">Calc.: N, 9.43; found, 9.50.</div>

In the same way finely crystalline salts of this acid with aniline and p-toluidine were obtained, but not with methyl and ethyl substituted aniline, diphenylamine or salts of hydroxylamine. When methylbenzyl aniline was treated with chloroacetic acid, benzaldehyde was formed.

$CO(NH_2)_2CH_2ClCO_2H.C_2H_5OH$.—Equivalent quantities of pure urea and monochloroacetic acid were brought together in absolute alcohol. Upon evaporation very large, leafy, transparent crystals were formed having a high luster. These upon standing constantly smelled of alcohol, which was given off until the crystals fell into a fine, white crystalline powder, evidently the anhydrous salt. Both crystals and powder are

very soluble in water, which, however, hydrolyzes the combination to some extent, since urea crystals form before the salt itself separates out. Calc.: N, 13.67; found, 13.60.

Basic Iron and Chromium Compounds.—No definite compounds were obtained by treating ferric and chromic hydroxides with water solutions of chloroacetic acid. The normal ferric salt appears to hydrolyze very easily, since even in cold solutions the iron is practically all removed by precipitating as a mixture of the basic salts. A solution containing the chromic salt was strongly dichromatic, green and purple; upon evaporation crystals of pure monochloroacetic acid were deposited. Later a pale green crystalline substance separated out and appeared to be a hydrate of $Cr(CH_2ClCO)_2OH$ mixed with a small amount of some salt more basic.

All of these salts, when treated in solution with silver nitrate, in no case gave more than a very slight opalescence.

None of the above salts are found mentioned in available literature.

A number of other compounds have been prepared and work is in progress upon still others.

MISSOULA, MONT

THE RESOLUTION OF ASCARIDOLIC ACID.

By E. K. NELSON
Received October 13, 1914

Ascaridolic acid,[1] possessing the structure of a 1,4-cineolic acid, should, like ordinary $d + l$ cineolic acid, be a racemic compound.

Attempts to effect its resolution by means of its brucine or strychnine salt resulted in failure. With the cinchonidine salt, however, little difficulty was experienced.

Twenty grams of ascaridolic acid were dissolved in 2500 cc. of hot water and 27 g. of powdered cinchonidine were gradually added while boiling and stirring. On cooling, a salt separated in the form of fine, silky needles, which, filtered, washed with a little water and dried, weighed 19 g., corresponding to 8 g. of the original acid. The mother liquors and washings were concentrated at a low temperature (not over 40°) and the salt separated was fractionally crystallized until it was fairly free from the difficultly soluble salt.

The cinchonidine salt of the acid was thus separated into a slightly soluble and a readily soluble salt. These salts, dissolved in warm water and decomposed with an excess of dilute hydrochloric acid, yielded the corresponding acids, both of which, after purifying by repeated crystallization, were obtained in well formed prisms.

[1] E. K. Nelson, THIS JOURNAL, **33**, 1410 (1911), **35**, 89 (1913).

The less soluble salt yielded d-ascaridolic acid. 2.0545 g. made up to 25 cc. solution in chloroform at 24° in 200 mm. tube = 2.29° to the right. $[\alpha]_D = + 13.93°$, melting point 129–130°.

The more readily soluble salt yielded the l-ascaridolic acid, which also melts at 129–130°.

2.0431 g. made up to 25 cc. solution in chloroform at 24° in 200 mm. tube = 2.25° to the left.

$[\alpha]_D = -13.77°$.

WASHINGTON, D. C

OPTICAL ROTATORY POWER AND CHEMICAL CONSTITUTION.

BY L. G. WESSON.

Pickard and Kenyon, in a series of valuable investigations on the "Dependence of Rotatory Power on Chemical Constitution,"[1] have determined the molecular rotatory power of over 100 closely related compounds. The list includes methyl ethyl carbinol and its homologs up to the ethyl tridecyl member, isopropyl methyl carbinol and its homologs up to the isopropyl decyl member, and the esters of the methyl carbinol series with the homologous n-aliphatic acids from acetic up to dodecoic, myristic, palmitic and stearic acids.

From these experimental results, which are to be made the basis of the present paper, Pickard and Kenyon derive an hypothesis[2] which is "based merely on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom" and "appears to explain the results obtained for the three series of carbinols, as well as those obtained for eight series of simple esters derived from the 'methyl' series of carbinols."

"In a homologous series of optically active compounds represented by Cabcd, the usual effect of increasing the size of d (representing the growing chain) is to alter in a regular manner (usually to increase) the molecular rotary power of the compounds."

"When the groups (or atoms) represented by a, b, and c occupy a relatively small space, as, for example, in the 'methyl' series of carbinols, $CH_3.CH(OH).R$, the values of the molecular rotary powers of the homogeneous compounds increase regularly with the increasing size of the chain, and only in solution are affected by the peculiar configuration of the chain, when this returns upon itself."

"When, however, the space occupied by the groups (or atoms) a, b

[1] Part I, J. Chem. Soc., 99, 45 (1911); Part II, Ibid., 101, 620 (1912), Part III, Ibid., 101, 1427 (1912); Part IV, Ibid., 103, 1923 (1913); Part V, Ibid., 105, 830 (1914); also, Ber., 45, 1892 (1912); Chem. News, 108, 163 (1913); and Trans. Faraday Soc., 1914 (C. A., 8, 2339).

[2] Part IV, J. Chem. Soc., 103, 1930 (1913).

and c is larger, the increase in molecular rotatory power may become less regular as d increases in size; either (1) it may be specially affected, when the chain returns on itself, as in the 'ethyl' series, $C_2H_5.CH(OH).R$, or (2) there may be a relatively large increase until d contains five carbon atoms with an increase of a much smaller order beyond; as, for example, in a series of esters, such as those of secondary octyl alcohol with normal aliphatic acids, in which there is a large increase in the value of the molecular rotatory power for each member of the series up to the normal valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the palmitate; or (3) when the space occupied by the groups a, b and c is still greater, an 'approximate maximum' is reached when the growing chain contains fewer than five carbon atoms; as, for example, for the carbinols of the isopropyl series, $CH(CH_3)_2.CH(OH).R$ (when these are examined in the homogeneous state), and in a series of n-dodecoates of the 'methyl' carbinols, $R.CH(OCO.C_{11}H_{23}).CH_3$, in both of which the values of the molecular rotatory power increases rapidly up to that for the member with R containing four carbon atoms with a much smaller increment for the higher members."

In brief, the differences between the curves for the various series are ascribed by Pickard and Kenyon to the differences in the amount of space occupied by the atoms or groups other than the growing chain, as well as that occupied by the growing chain itself.

P. F. Frankland, to whom so much is due in the field of optical activity, expressed an opinion very similar to the above in 1912.[1]

"It might at first sight be supposed," says Frankland, "that if such steric interference (in compounds with a chain of 5 carbon atoms attached to the asymmetric one[2]) were the cause of this limitation (in the increase or decrease of the molecular rotatory power), the maximum or constant molecular rotation should always occur at the same term in all homologous series. This, however, is not found to be the case, and it would appear probable that the term at which such interference occurs will depend, not only on the length of what may be called the homologous chain itself, but also on the other groups, which are present in the molecule, and which may themselves interfere with the normal development of the homologous chain. * * * * More recently, Pickard and Kenyon have prepared a similar homologous series from isopropyl carbinol, and in this it might be anticipated that the isopropyl group should give rise to more interference than the methyl group in the previous series."

The writer believes that these phenomena, explained by Pickard and

[1] Presidential address, *J. Chem. Soc.*, **101**, 654 (1912).

[2] Frankland early recognized the special influence of carbon chains with 5 (or 6) and 9 (or 10) carbon atoms in phenomena of optical activity. See *J. Chem. Soc.*, **75**, 368 (1899).

Kenyon and by Frankland on the basis of the space occupied by the groups attached to the asymmetric atom and their interfering influence upon each other, should rather be ascribed to another factor, namely, the attractive forces exerted by the groups upon the asymmetric atom.[1]

If these tables and curves, compiled from Pickard and Kenyon's experimental work, be examined, the following significant facts will be observed

1 The molecular rotation of the series of ethyl carbinols (Table I and Fig 1) has a smaller value throughout than has that of the methyl series, while both the methyl and ethyl series have smaller values than the isopropyl series

TABLE I —MOLECULAR ROTATORY POWERS OF THE NORMAL SECONDARY ALCOHOLS [2]

$[M]_D^{20}$	In the homogeneous state			Dissolved in ethyl alcohol [4]		
	Methyl [3]	Ethyl [4]	Isopropyl [3]	Methyl	Ethyl	Isopropyl
Methyl	0°	10 30°	4 3°	0°	10 77°	4 70°
Ethyl	10 3	0	15 4	10 77	0	16 73
n-Propyl	12 1	2 01	24 7	13 60	1 17	27 07
n-Butyl	11 8	9 43	33 3	12 95	11 17	35 97
n-Amyl	12 0	10 69	32 9	13 28	14 47	38 24
n-Hexyl	12 7	10 63	33 9	12 73	13 86	38 36
n-Heptyl	12 9	10 58		13 10	9 81	
n-Octyl	13 7	10 74	34 5	14 04	10 69	39 99
n-Nonyl	14 0	11 09		13 95	11 35	
n-Decyl	14 5	12 44	34 5	14 76	13 46	39 38
n-Undecyl	14 4	12 56		14 74	13 38	
n-Dodecyl		12 61			12 44	
n-Tridecyl		12 38			12 75	
n-Pentadecyl		12 88			12 99	

[1] The attention of the writer has been recently called to a significant sentence by Michael, Ber , 34, 3647 (1901), J prakt Chem , [2] 75, 117 (1907), in which he states that carbon asymmetry is to be considered the result of the chemical-mechanical influence or tension of four unequal forces on an atom, rather than a purely chemical effect

Doubtless the idea that optical activity may be due to differences of forces of attraction for the asymmetric atom has also occurred to others

A little different are the theories of Baly and Winther

Baly, Z Elektrochem , 17, 211 (1911), believes that optical activity is due to the asymmetric field caused by the merging of the lines of force from the residual affinities of the groups about the asymmetric atom

Winther, Z physik Chem , 60, 590 641 756 (1907), claims that every change in the optical rotation of a substance is connected as effect to cause with a volume change, and every volume change, due entirely and solely to a pressure change (internal or external) is accompanied by a proportional change in the optical rotation

[2] In Figs 1 and 2 which represent the table, the curves have been drawn to show only the variations common to both the homogeneous and dissolved states

[3] Pickard and Kenyon, J Chem Soc , 99, 49 (1911)

[4] Ibid , 103, 1925 (1913)

[5] Ibid 101, 624 (1912)

[6] Ibid 103, 1957-8 (1913)

TABLE II.—MOLECULAR ROTATORY POWERS OF THE ESTERS OF THE METHYL CARBINOLS [1]

$[M]_D^{20}$ of the ester of

	Me ethyl carbinol	Me propyl carbinol	Me butyl carbinol	Me amyl carbinol	Me hexyl carbinol	Me nonyl carbinol
Acetate	29 70°	22 30°	14 59°	13 00°	11 77°	11 28°
Propionate	31 00	23 66	15 43	14 40	12 99	11 75
Butyrate	31 63	24 92	18 62	18 91	17 90	17 68
Valerate	32 74	27 54	20 75	20 52	19 60	19 09
Hexoate	32 10		21 68	21 34	20 42	19 91
Heptoate	32 31		22 17	21 72	20 78	20 37
Octoate	32 28			21 95	21 12	
Nonoate	32 17		22 69	22 26	21 50	21 25
Undecoate	32 48		22 55	22 59	21 91	21 43
Dodecoate	32 48	28 19	22 68	22 58	21 84	21 91
Myristate	32 21		23 10	22 52	22 40	21 87
Palmitate	31 99			23 10	22 57	
Stearate	31 92			23 15	22 61	

Fig 1

CARBINOLS

In homogeneous state

Carbon atoms in growing chain
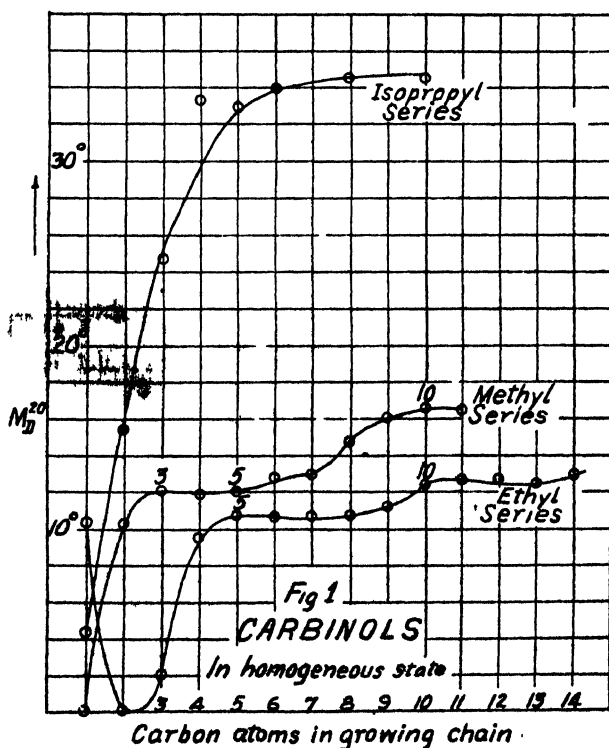
[1] Pickard and Kenyon, J Chem Soc , 105, 831 (1914)

2. In the *ethyl* series of carbinols there are found exaltations in the curve at the points at which the growing chain contains 5 or 10 carbon atoms, and is therefore of the most favorable length to return upon itself toward the asymmetric atom. This exaltation for the ethyl carbinols is much more pronounced when the rotatory power is measured upon the solution of the carbinols (Fig. 2), and solution has been found in general to bring out and magnify such effects.[1]

Fig. 2
CARBINOLS
Alcoholic solution.

Carbon atoms in growing chain.
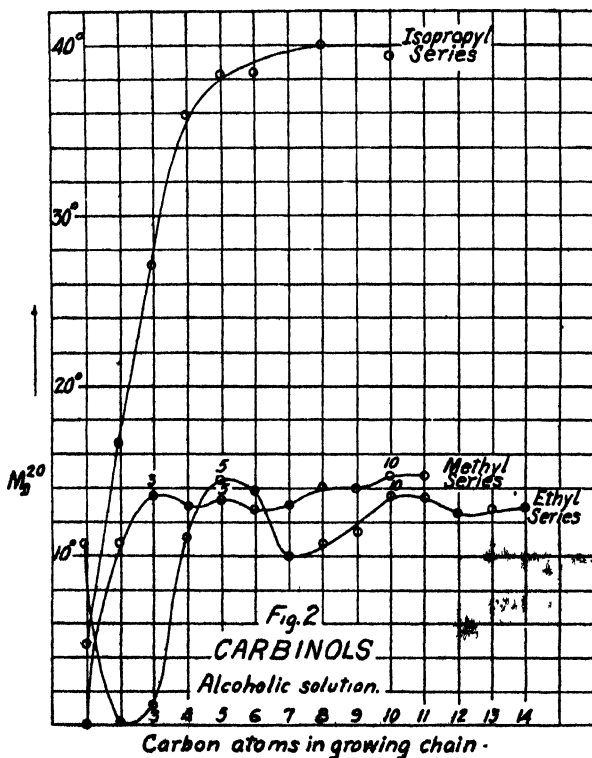
In the *methyl* series such an exaltation cannot be detected at the points 5 and 9, or 10, until the carbinols are dissolved, while in the *isopropyl* series even solution is not sufficient to bring out a corresponding exaltation.

3. In the curves of the esters (Table II and Fig. 3), if the acid is kept constant in each curve and the alkyl radical gradually increases, an exaltation is found when the alkyl group contains 5 carbon atoms.

In the corresponding curves in which the alkyl radical is kept constant

[1] Frankland, *J. Chem. Soc.*, **101**, 660 (1912); Pickard and Kenyon, *Ibid.*, **103**, 1928 (1913).

in each curve and the length of the acid chain gradually increases (Table II and Fig 4), an exaltation is found when the acid contains 4 and 5 carbon atoms.

4. In all of these series of curves, the exaltations become, in general, less marked as the value of the molecular rotatory power increases

Fig. 3.

ESTERS of the CARBINOLS

$R_y CH_2 \overset{*}{C}HOR_c$

Carbon atoms in chain of R_y ⟶
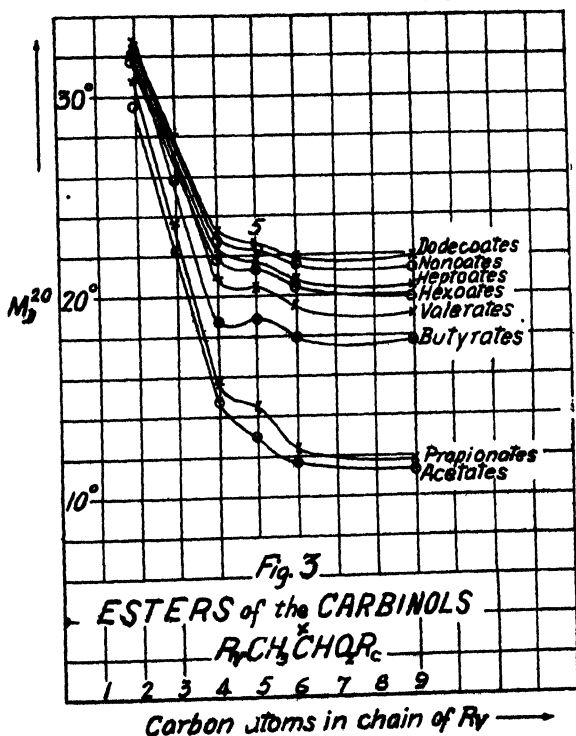
According to the hypothesis supported in this paper these regularities are to be accounted for by the following considerations:

1. The alkyl radicals in general, as is shown by their chemical behavior (*e. g.*, dissociation constants of the aliphatic acids) in a number of various types of compounds, experience a much sharper transition in properties as one passes from the methyl to ethyl than from the ethyl to propyl group, likewise a greater transition occurs from ethyl to propyl than from propyl to butyl, and so on.

One of the properties, which thus changes, is the positivity of the alkyl radical[1] toward such a group as for example—CRHOH of the optically

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[1] Michael, *J. prakt. Chem.*, [2] 60, 286 and 409 (1899); *Über einige Gesetze und deren Anwendung in der organischen Chemie.* See especially p. 432 in this connection.

active compounds which we are considering. The methyl group will exert upon the central carbon atom of this group an attractive force which will differ more from that of an ethyl group than would an ethyl and isopropyl group when compared in the same way. Propyl and butyl likewise differ, but to a less extent than do ethyl and propyl. As the alkyl radical increases in length, the differences between the relative positivity of the successive homologs decreases. Similarly, between a normal alkyl radical such as propyl and a branched one as isopropyl, a still greater difference of attractive force would be expected.[1]

Fig. 4

ESTERS of the CARBINOLS

$R_c CH_3 CHQR_V$

Carbon atoms in chain of R_V
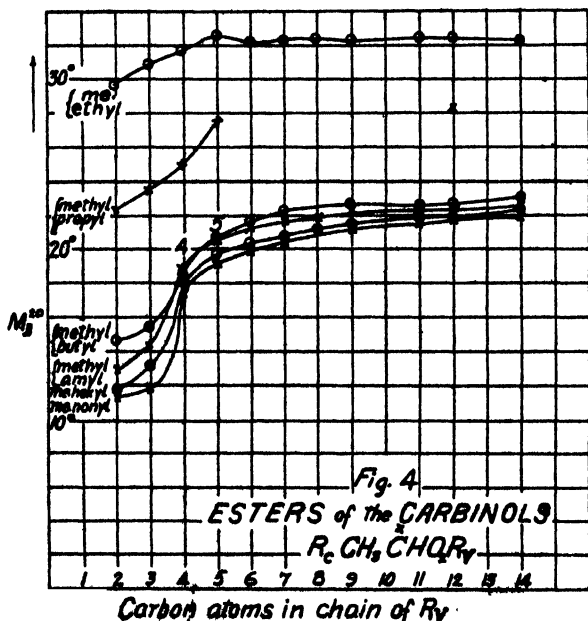
We have then in the ethyl series from ethyl propyl carbinol on, two alkyl groups united to the asymmetric atom, which differ less in the respective forces with which they attract that atom than do the corresponding groups in the methyl carbinol series. The optical rotatory power of the ethyl carbinol series is, therefore, smaller than that of the methyl series.

In the isopropyl series this difference is still greater than in the methyl carbinols (e. g., isopropyl and ethyl, isopropyl and propyl, etc.), and we find that the rotatory power is correspondingly much larger than in the two preceding series.

2. In discussing the attractive forces, the attraction of a group as a whole should be considered rather than that represented by the particular

[1] Michael, loc. cit., p. 432.

atom which happens to be adjacent to the asymmetric one. Thus all of the atoms perform their share to a degree which depends upon their position in the molecule.[1] This effect may be exerted through other atoms or through space, the combined influence in alkyl radicals decreasing in the order 2-3-5-6-4-7-(9-10-11)-8.

The atoms 5 and 6 owe their unexpectedly great influence to the fact that they occupy a position in which they are able to approach comparatively near atom 1 as the growing chain in its natural configuration returns upon itself. This sudden increase of attractive force is necessarily small in comparison with the total force exerted by the group for the asymmetric atom, yet if two of the groups are nearly equal this change may be quite appreciable in comparison with the already existing difference, and, as in the ethyl series, quite an appreciable exaltation in the rotatory power may be observed at this point.

In the methyl series, where the difference between the attractive forces of the two alkyl groups is greater, the sudden increase due to the close approach of atom 5 to the asymmetric atom is much smaller in comparison with the already existing difference. The effect of this secondary influence on the optical activity is therefore so small that it is observable only when the carbinols are in a dissolved condition.

The difference between the alkyl groups is already so great in the isopropyl series that no appreciable effect is produced on their relative values by the return of the alkyl chain upon itself, and, as would be expected, no exaltation can be observed at this point in the case of the isopropyl series, even if the measurements are made upon the dissolved substance.

3. Similar considerations are applicable in the case of the esters of the carbinol. The return of the chain upon itself produces an additional attraction of the whole group for the asymmetric atom, and, therefore, a point of inflection in the rate of change of the optical activity.

If, as in Fig. 3, the normal alkyl group united to the asymmetric atom is gradually increased in size, an exaltation is found at the point corresponding to a chain of five carbon atoms, whereas, if the acyl group is similarly lengthened, an exaltation is found when the total chain united to the asymmetric atom consists of one oxygen and four or five carbon atoms.

4. If optical activity is dependent, as claimed, upon differences in the attractive forces exerted by the atoms or groups for the asymmetric atom, the smaller the difference between two of the groups, other differences being constant or practically so, the smaller will be the optical

[1] Michael, *Loc. cit.*, pp. 331 and 335. THIS JOURNAL, **34**, 849 (1912). The literature contains many investigations which demonstrate the marked influence of the position of substituents on optical activity. See, *e. g*, Rupe, *Ann.*, **369**, 311 (1909).

rotatory power. Thus, the smaller the rotatory power, the greater would
be the expected effect upon this by a given small change in the difference
between the attractive forces of these two almost equal groups. The
observed facts indicate it to be a general rule that as the molecular rota-
tory power decreases in a group of curves the exaltations or other uni-
form deviations become increasingly large.

Product of Asymmetry.

The data at hand are not sufficient to indicate whether or not the molecu-
lar rotatory power is a function of the product obtained by multiplying
together the differences between the attractive forces exerted by the four
atoms or groups upon the asymmetric atom; that is,

$$F \ (A-B) \ (A-C) \ (A-D) \ (B-C) \ (B-D) \ (C-D)$$

As each atom or group affects the character (positivity) of the asymmetric
atom, it is likely that a given atom or group would possess no constant
value in this relation even when very similar compounds are compared.
It is therefore not at all surprising that repeated attempts to derive con-
stants for the various radicals and atoms have not met with success.[1]

Effect of Mass on Optical Activity.

That the mass of an atom or a group united to the asymmetric atom may
be of some significance in determining its effect upon the optical activity
of the molecule is not excluded by the theory of attractive forces. At
the best, however, the effect of mass seems to be only auxiliary to the
larger one of relative attractions. Examples of this are familiar in the
literature of optical activity.

A possible mode may be suggested here by which the asymmetry of
the attractive forces exerted upon an asymmetric atom may be con-
ceived to be connected with its effect upon the plane of polarization of
light.

If, in a symmetrical molecule of the type $M a a b c$ a, plane were passed
through atoms M, b and c, the atoms a and a would be symmetrically
situated with respect to the plane $M b c$. The atoms in a molecule, in
their oscillations toward and away from each other must move in paths
which express the resultant of all the forces which are exerted upon them.
Therefore, in a molecule of the type $M a a b c$, one can be certain that the
path described by M will either lie in the plane $M b c$, or, if it does not do
this, it will, as a and a are alike, lie on the average or the same extent

[1] Compare this product with a, the product based on asymmetry of mass; Crum
Brown, *Proc. Roc. Soc. Edinb.*, **17**, 181 (1890); Ph. Guye, *Compt. rend.*, **110**, 714 (1890);
b, the product based on empirical constants for various atoms and radicals; Bose and
Willers, *Z. physik. Chem.*, **65**, 695 and 702 (1909); Walker, *J. Phys. Chem.*, **13**, 574
(1909).

on one side of this plane in one half of the total number of molecules as
it does on the other side of the other half.

In an asymmetric molecule, however, represented by $M\ abcd$, the path
of M would not be expected to average the same in one
direction in one-half of the total number of molecules as
it does in the other direction in the other half, unless an
equal number of the stereo-chemically opposite molecules
$M\ bacd$ be present with the molecules $Mabcd$.
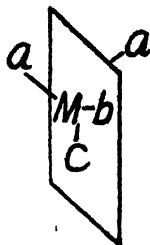
To the mean asymmetric path taken by the asymmet-
ric atom (carrying an electric or magnetic field)[1] is as-
cribed the optical rotatory power of the asymmetric mole-
cule. Any influence which increases the effective asym-
metry of this orbit will, according to this hypothesis, increase the ob-
served molecular rotatory power of the substance.

A theory which attempts to point out the cause of the phenomenon of
optical activity must fulfill at least this important condition—it must ac-
count for an asymmetry such that polarized light passing through the
molecules of an active substance in one direction is affected to a greater
degree than in the other. The postulate just described of the asymmetric-
ally moving atom answers this requirement in the following way:

Let the motion of the asymmetric atom be simplified at any given in-
stant, and during the time required for the passage of a light wave through
the space under its influence, to the form of a portion of a helix, the whole
helix, of which this is a portion, representing not the actual path of the
atom, but rather a basis on which the portion may be considered in com-
parison with the asymmetric atoms of the other molecules.[2]

Consider an active substance which has been completely resolved into
its optically opposite components. and which, therefore, contains only those
molecules possessing one of the two possible optical configurations.
At any instant, the asymmetric atom, M, is moving in one-half the total
number of molecules in one general direction, e. g., toward atom d, with
a motion whose resultant toward d will require a mean of s turns and time t
for completion. In the other half, the motion of M in the same instant
is away from atom d, and is represented by turns s' and time t'. Of
the first, one-half of the molecules will face in one general direction and
the general direction of the propagation of the light will coincide with that

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[1] See especially, in this connection, P. de Heen, *Bull. Acad. roy. Belgique, Classe
des Sciences*, 1913, p. 680; *Chem. Zentr.*, 1914, I, 599.

[2] The whole motion of the asymmetric atom may, perhaps, according to this con-
ception, be described as following a curved orbit with a simultaneous forward motion,
the axis of the orbit at the same time turning eventually toward every conceivable
direction. The familiar wound ball of twine furnishes a homely illustration of this
path. The harmonic motions finally run their course, the atom arrives again at its
starting point, and is ready to repeat its complex revolution.

of the motion of M. In the other half of this group, the light and atom will be moving in opposite directions, and, as the light must occupy a finite time in its passage through the field of influence of M, the effect of M on the light will be greater in those molecules in which the two directions coincide than can be compensated for by the equal number of molecules facing in the opposite direction in which the light and the atom approach each other and pass, but do not move together. Thus, for the molecules in which M is in motion *toward d*, there will be a resultant uncompensated effect upon the light.

The same holds true in a similar way for the molecules in which M is in motion *away* from *d*, but the effect which is caused by an atomic motion represented by s' turns and time t' will be different in amount from that caused by the first group. Thus a net rotation will be observed upon the emergent light.[1]

Conclusion.

The hypothesis here presented was worked out by the author in 1912. At that time no mention could be found that such an hypothesis had ever been suggested to account for the phenomena of optical activity, or, in fact, since, has one been found in the literature devoted to optical activity. The recent experimental results of Pickard and Kenyon, forming as they do, such a complete series of comparable data, have been used in the preceding paper to the exclusion of other and less conclusive results upon which previous deductions had rested. These offer for the first time an indication of the validity of the hypothesis that the phenomena of optical activity depend primarily upon an asymmetry of the attractive *Forces* exerted upon an asymmetric atom by its four adjacent atoms or groups.   .

CAMBRIDGE, MASS.

THE OCCURRENCE AND SIGNIFICANCE OF MANGANESE IN THE SEED COAT OF VARIOUS SEEDS.

BY J. S McHARGUE.

It has been observed by investigators that the different organs of some plants show considerable variation in the amount of manganese they contain. According to the researches of Jadin and Astruc,[2] the

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[1] The possibility of the existence of optically active individual *symmetrical* molecules is suggested by the above, according to which a symmetrical and an unsymmetrical molecule may differ only in that the former produces an effect on the light which is compensated for by other molecules while the latter produces an uncompensated effect.

[2] Jadin and Astruc, *Compt. rend.*, 156, 2023 (1913).

aerial portions of plants contain more manganese than the subterranean. Pichard[1] also states that the seeds of plants are quite rich in this element.

While making some investigations on the occurrence of barium in plants,[2] in the spring of 1913, the writer observed that the ash of hazelnut shells emitted a distinct odor of chlorine upon the addition of hydrochloric acid, thus indicating the presence of manganese in the ash. This observation suggested an investigation on the amount of manganese in plants in general, and, in particular, as to the occurrence of this ele-

TABLE I

Name of material	Per cent of Mn in the material dried at 100°
Brown hulls of apple seed	Trace
Seed coats	0 0165
Kernels of apple seed after removing the skin	Trace
Brown hard shell of peach seed	0 0005
Brown skin off kernels	0 0110
Kernels of peach seed after removing skin	0 0019
Chestnut hulls	0 0106
Chestnut kernels after removing skin	0 0042
Horsechestnut brown hulls, including inner coats	0 0022
Kernel of horsechestnut	Trace
Walnut, outside or soft hull	0 0015
Walnut hard shells	c 0006
Walnut skin off kernels	0 0100
Walnut, kernels, after removing skin	0 0033
Acorns	
Burr oak, outside shells	0 0088
Burr oak, brown skin covering kernels	0 0110
Burr oak, kernels, after skin was removed	0 0015
Cottonseed hulls	0 0026
Cottonseed meats	0 0018
Brazil nuts, hulls	0 0018
Brazil nuts, brown skin	0 0145
Brazil nuts meats without the skin	0 0011
Almond, outer shell	Trace
Brown skin covering kernels	0 0044
Kernels, without skin	0 0009
Cocoanut, hard hull	Trace
Cocoanut, brown skin covering meat	0 0048
Cocoanut, meat, without the skin	0 0022
Cocoanut, milk	0 0002
Butter beans, skins off cotyledons	0 0037
Butter beans, cotyledons, without skin	0 0018
Wheat bran	0 0194
Wheat flour	0 0055
Corn bran	0 0011
Corn meal	0 0001
Onion	Trace

[1] P Pichard, *Ibid*, 126, 1882 (1898)

[2] THIS JOURNAL, 35, 826 (1913)

ment in the different parts of various nuts and seeds. Qualitative tests showed that manganese could be readily detected in the different parts of seeds, and closer examinations revealed the fact that certain coats surrounding the kernel contain very notable amounts of this element. Therefore, a number of analyses have been made for the purpose of showing the amount of manganese present in the different parts of the seeds of various plants. The results are given in Table I and indicate the percentage of the element manganese in the dry material.

The results in the table show considerable variations in the amount of manganese contained in the different parts of seeds of the same plants. It is to be observed that the seed coat immediately surrounding the kernel or cotyledons of seeds contains a considerably larger proportion of manganese than either the kernel or the outer epidermal coats. This concentration is especially noteworthy in the apple, peach, black walnut, acorn, Brazil nut, chestnut, almond and wheat bran. Wherever it was possible to dissect this thin membrane, usually brown in color, from the cotyledons to which it is attached, in sufficient amount for analysis, it invariably showed a higher concentration of manganese than any of the other parts of the seeds tested.

The chief interest in this connection lies in a plausible explanation of the function of the manganese at this particular point. The occurrence of manganese in this connection appears to be indicative of important biological relations, rather than a mere accumulation of either waste material or plant food.

In 1895, De Ray-Pailhade[1] observed the presence of laccase, an oxidase, in the seeds of a rather large number of different plants. In 1897, Bertrand[2] pointed out that laccase, an oxidase, obtained from the juice of alfalfa (*Medicago sativa*) contained considerable quantities of manganese, and has subsequently shown that small amounts of the salts of this element stimulated the oxygen-carrying power of the oxidizing enzymes and, therefore, concludes that this element has important biological functions in plant metabolism.

Since manganese has been shown to occur in unequal proportions in the different parts of plants and seeds of those plants, experiments were planned with the hope that some parallelism could be established with respect to the manganese content and the presence of oxidases in the different parts of the plants under investigation. In these experiments parts of raw plants were prepared and tested for the presence of oxidases by grinding a 1 g. portion with 10 cc. of distilled water, filtering through a dry filter into a clean test tube, without washing, and adding 2 cc. of a guaiacum solution. The color that developed was noted as "strong,"

[1] J. De Ray-Pailhade, *Compt rend.*, 121, 1162 (1895).

[2] G Bertrand, *Ibid.*, 124, 1355 (1897).

"moderate," "trace," and "none." The remaining portions of the same plant were then dried, ashed, and the manganese determined. The results obtained in a number of plants are given in Table II.

TABLE II

Material	Per cent of Mn in the substance dried at 100°	Guaiacum test for oxidases
Irish potato peelings	0 0400	Strong test
Cubes cut from the center of the potato	0 0009	Trace
Brown hulls of apple seeds	Trace	Moderate
Seed coat	0 0165	Strong
Kernels	Trace	Trace
Sweet potato peelings	0 0075	Strong
Cubes cut out of the center of same potato	0 0020	Trace
Turnip tops	0 0900	Strong
Peelings off roots	0 0024	Moderate
Root meats	0 0009	Trace
Carrot tops	0 0062	Strong
Peelings off roots	not est	Strong
Meat of roots near center	not est	Trace
Onions bulbs	Trace	None

While the results on the presence of oxidases in the above experiments are only qualitative, they are of sufficient importance to indicate a close relationship existing between the amount of manganese present and the depth of color produced by the guaiacum reaction for oxidases. In every case where manganese was found in appreciable amounts, a corresponding positive result was obtained for the presence of oxidases, and the absence of manganese was accompanied by negative reactions for oxidases. In these experiments it is shown that neither manganese nor oxidases are evenly distributed in the tubers and roots of potatoes, turnips or carrots, each being largely confined to the outer epidermal layers, thus indicating a close relationship between manganese, oxidases and free oxygen in the soil. In the case of the apple seeds very interesting results were obtained, inasmuch as they throw considerable light on the accumulation of manganese in the seed coats of different seeds and nuts. The seeds from a ripe apple were separated into three parts, the outer brown hull, the seed coat and the kernels, and each tested for the presence of oxidases. The outer brown hull showed a moderate blue coloration with guaiacum, the seed coat showed a strong blue coloration, and the kernels showed only a trace. A determination of manganese in each of these parts showed a larger proportion of this element in the seed coats than in the brown hulls, and only a trace in the kernels. Similar results with respect to manganese were obtained on the seed coats of the acorn, almond, black walnut, chestnut, Brazil nut, wheat bran, etc., all of which were not obtainable in the green or mature stages of growth at the time the investigation was being carried on. However, all of the last named

plants are morphologically akin to the apple with respect to their seed coats.

A search through the literature upon the function and chemistry of the seed coats of various plants shows that no work has been done on this subject, and that botanists have thus far been unable to attribute any important function to this membrane in its relation to the embryo. From the above data, in connection with the researches of Bertrand and others, it is evident that a close relation exists between manganese and oxidases in plants. May we not also assume that the accumulation of manganese in the seed coat sustains a very important relation to the oxidizing enzymes in this part of the seeds? It is very probable that these enzymes have much to do with the selection, compounding and storing away of the reserve material in the kernels of seeds.

It has also been shown that fatty seeds absorb large quantities of oxygen during germination. De Ray-Pailhade[1] has shown that there was an increase in the presence of oxidases as the germination progressed. He further noted that, in the presence of laccase and free oxygen, philothion is converted into carbon dioxide, and thereby contributes to the respiration of the embryo plant.

It is therefore probable that the manganese in the seed coat also assists in stimulating the enzymes which split up the fats, sugars, starches, etc., and render them more readily available for the young seedling during the early stages of its growth.

If such be the function of manganese in plants, we must conclude that it bears a very important relation to the vital processes in seed formation and germination.

Lexington, Ky

THE BITTER PRINCIPLE OF COMMON RAGWEED.

By Burt E Nelson and George W Crawford

As part of a pharmacological study of ragweed, *Ambrosia artemisifolia*, Linn., Order *Compositae*, with a view to learning something of its supposed therapeutic value in the treatment of certain types of hay fever, it became desirable to isolate the bitter principle.

This was accomplished by extracting ten kilos of the partially air-dried drug with alcohol, distilling off the latter at a gentle heat, mixing the soft aqueous residue with more water and some aluminium hydroxide cream for separating the "resinoids," and, after removing the latter by filtration, clearing and defecating the aqueous filtrate by a slight excess of lead acetate. The remaining liquid was repeatedly extracted by ether

[1] J. De Ray-Pailhade, *Compt. rend.*, 121, 1162 (1895).

until the bitter taste was but slightly apparent (about twenty-five times in all) and the ether recovered by distillation.

As the remaining residue was still quite highly colored, an attempt was made to still further purify it by solution in alcohol, addition of water and boneblack, and filtration after some hours' digestion with the latter. On evaporation and careful drying, the remaining residue was quite deep amber colored, and on long standing in a desiccator formed a mass of fine white needle-shaped or prismatic crystals, distributed through a much larger quantity of the amber colored amorphous body.

The two were finally separated by fractional solution with ether, in which the amorphous body is the more readily soluble. Repeated separations are necessary in order to effect purification by this means. As finally obtained, the amorphous amber-colored body was distinctly bitter in a one to ten thousand solution, while the white crystals were tasteless and, aside from being somewhat sternutatory when inhaled, inert physiologically as far as we were able to determine from the small amount on hand. These crystals melted sharply at 208° (uncor.), and gave on analysis:

Carbon, 69.13, 69 25; hydrogen, 7.77, 7.78; oxygen, 23.10, 22.97%

With strong sulfuric acid they give an orange color which becomes bright crimson, especially on warming. Yield, 0.02%.

The bitter, amorphous, amber-colored body finally becomes indistinctly crystalline on long standing in a desiccator. It melted indefinitely at from 65–70° (uncor.), and gave on analysis:

Carbon, 68.89, 68.38; hydrogen, 7.78, 7.60; oxygen, 23.33, 24 02%

We did not have sufficient material purified to allow of repeating this analysis a third time.

A molecular weight determination by the freezing point method, in acetic acid, gave 523. With strong sulfuric acid, the material gives a brownish color becoming brownish purple, and with Froehde's reagent, greenish. Fehling's solution is slowly reduced by the body after hydrolysis. Yield, 0.10%.

As the above results agree with the data given in the literature for absinthin, the bitter principle of wormwood (*Artemesia absinthium*, Linn., Order *Compositae*), we have also separated some of the latter according to the above method. The appearance of this absinthin was entirely similar to that of our amorphous bitter principle from ragweed. It was not, however, accompanied by any white crystalline body. It melted indefinitely at from 65–68° (uncor.), and gave on analysis:

Carbon, 68.13, 68.19; hydrogen, 7.59, 7.62; oxygen, 24.28, 24.19%
Molecular weight by the freezing point method, 523

It also gave the brownish color, becoming purplish with strong sulfuric acid, and greenish with Froehde's reagent. Like the bitter principle

from ragweed, it also slowly becomes indistinctly crystalline on long standing in the desiccator, and slowly reduces Fehling's solution.

Conclusions.

In view of the uncertainty attending the accurate analysis of an amor-. phous body of this kind, we believe that the results obtained from the analysis of the bitter principle of common ragweed and of absinthin from wormwood justify us in concluding that the two bodies are probably identical. Other pharmacological studies tend to show that the use of preparations of ragweed in the treatment of hay fever is based on irrational grounds.

LABORATORY OF THE NEW YORK STATE HOSPITALS,
BINGHAMTON, N Y.

THE VOLATILE OILS OF THE GENUS SOLIDAGO.

By EMERSON R MILLER AND MILNER H. ESKEW.

The genus Solidago is represented in the United States by about seventy-five species. Some of these occur quite abundantly but can, as yet, scarcely be considered of any economic importance. A few have been used medicinally, particularly *Solidago virgaurea* Linn., which is common to Europe and North America, and *solidago odora* Ait., which was at one time recognized by the United States Pharmacopoeia. The root of *Solidago canadensis* L. is said to contain a coloring matter once used in Canada as a valuable dye.

Very little is known about the chemistry of the plants of this genus. Volatile oils have been obtained from four species, but with the exception of the oil of *Solidago canadensis* L. nothing is known about their chemical composition. According to Schimmel & Co.,[1] the constituents of the last named oil are *pinene* (85%), *phellandrene, dipentene, limonene, borneol* (9.2%), *bornyl acetate* (3.4%), and *cadinene*.

The Volatile Oil of Solidago Nemoralis.

Solidago nemoralis Ait. is one of the smaller species of the genus, growing from Quebec to the North West Territory, south to Florida, and west to Texas and Arizona.

In their report of April–May, 1906, page 63, Schimmel & Co. give the following description of a sample of oil of *Solidago nemoralis* which they received from America: "The bright olive-green oil had a peculiar odor, reminding somewhat of cypress oil. The constants were: d_{15}• 0.8799, α_D —23° 10′, ester number 14.4, ester number after acetylation 38.2. The oil formed a cloudy solution in about seven and more volumes of 95% alcohol."

[1] *Report*, April, 1894, p. 57.

The oil used in our investigation was prepared by steam distillation from the fresh herb (root excluded) collected, mainly, in the flowering stage during the month of October   Ten samples were obtained, the percentage yield and optical rotation in a 100 mm. tube were as follows

No of sample	Yield Per cent	Optical rotation	No of sample	Yield Per cent	Optical rotation
1	0 34	$- 17\ 73°$	6	0 31	$—14\ 82°$
2		$—16\ 92°$	7	0 30	$—16\ 35°$
3	0 24	$- 16\ 60°$	8	0 33	$—15\ 77°$
4	0 316	$—16\ 64°$	9	0 33	$—15\ 73°$
5	0 43	$—15\ 73°$	10	0 30	$—15\ 70°$

The average per cent yield was 0 322

The investigation was carried out upon the mixture of these samples

Physical and Chemical Properties of the Oil.

In color and odor the oil was similar to the sample described by Schimmel & Co., quoted above, but in other respects differed considerably from that oil, as is seen from the following data $d_{25°}^{25°}$ 0 8532, $\alpha_D - 16\ 17°$, $n_D\ 18°$ 1 47397. Soluble in about four volumes of 90% alcohol, in about 24 volumes of 70% alcohol   Saponification number, 5 6, after acetylation, 9 4.

Test for Phenols. −5 cc of the oil were shaken in a cassia flask with an excess of 5% potassium hydroxide solution and enough water then added to bring the oil into the graduated neck of the flask. The diminution in volume was very slight, approximately 0 03 cc, corresponding to 0 6% of phenol. But the total amount of phenol subsequently separated from the oil was less than this.

Test for Ketones and Aldehydes —With Schiff's reagent no coloration was produced within two minutes. With phenyl hydrazine only a very slight cloudiness was produced   The oil may, therefore, be said to be practically free from aldehydes and ketones.

Saponification and Fractionation of the Oil.— The total quantity of oil was shaken several times with a 3% solution of potassium hydroxide, and, after the aqueous alkaline liquid was separated as completely as possible, the oil was heated about three-quarters of an hour on a boiling water bath with an excess of 0 5 N alcoholic potassium hydroxide solution. The greater part of the alcohol was then distilled off on a water bath and the contents of the flask diluted with a large volume of water. The oil, which separated, was removed from the alkaline liquid, washed until free from alkali, dried with anhydrous sodium sulfate and subjected to fractional distillation under a pressure of 23 mm. The fractionation was carried out three times. Fractions having the following constants were obtained·

Fraction	Boiling temperature	Rotation in 100 mm tube	Sp gr at $\frac{25°}{25°}$
1	57–59°	—19 5°	0 8525
2	59–61°	—13 28°	0 8607
3	61–72°	+ 7 86°	0 8609
4	72–80°	+45 87°	0 8610
5	80–100°	+43 46°	0 8923
6	100–120°	—12 83°	0 9226
7	Residue		

Identification of Pinene —Fractions No. 1 and 2 constituted the main portion of the oil.   When distilled under diminished pressure the greater part of Fraction No. 1 boiled between 159° and 165°   From this distillate a nitrosyl chloride was prepared both by the method of Wallach[1] and that of Ehestaedt,[2] the melting point of the product being 102–103°.   From the nitrosyl chloride a nitrol piperidide was prepared having the melting point 118–119°.

The alcoholic distillate recovered from the saponification mixture was diluted with a large volume of water   The oil which was thus thrown out of solution was separated, washed, dried, and found to have the following constants   B. p., 161–165°, α_D, —19 37°, $d_{25°}^{25°}$, 0 8523

This liquid was also identified as pinene by the preparation of a nitrosyl chloride, m. p 103°, and a nitrol piperidide, m p 118 119°.

A nitrosyl chloride was also prepared from Fraction No 2, but the yield was smaller

Examination for Phellandrene —Fraction No 3 was tested for phellandrene by Wallach's method for the preparation of phellandrene nitrosites but with negative results.   Fraction No 4 was tested in the same manner, but it also yielded no nitrosite

Examination for Borneol —Since the maximum boiling point of Fraction No 5 is near that of borneol and the odor of this fraction was somewhat suggestive of that of borneol, an attempt was made to prepare borneol phenyl urethane by means of carbanil, but the results were negative. Fraction No. 6 was also treated in the same manner but likewise with negative results.

A further attempt to identify borneol was made as follows the remainder of Fraction No 5 and a part of Fraction No. 6 were mixed and distilled under ordinary pressure.   The portion which came over between 195° and — was oxidized by means of chromic acid mixture, the acid liquid neutralized with sodium carbonate and then distilled with steam.   There was indication of the separation of camphor in the condenser, though the distillate had a somewhat camphoraceous odor.   This oil was treated with hydroxylamine hydrochloride in order to see if camphor

45, 251 (——)
Report of Schimmel & Co , April, 1910, p 164

oxime could be prepared. The thick, oily mass which was obtained had an odor very suggestive of camphor oxime and a few crystals had separated, but at the time of this writing the amount was insufficient for a melting point determination.

Examination for Camphor.—The remainder of Fraction No. 6 was treated with hydroxylamine hydrochloride but no oxime could be separated, indicating the absence of camphor.

Examination for Phenol.—Identification of Salicylic Acid. The aqueous alkaline liquid obtained by shaking the oil with 3% solution of potassium hydroxide was acidulated with dilute sulfuric acid, shaken out with ether and the ether allowed to evaporate. A thick, brownish red liquid was thus obtained from which, after standing some time, needle shaped crystals separated in very small amount. This substance gave an intensely violet color with aqueous ferric chloride solution. When treated with methyl alcohol and sulfuric acid it gave the odor of methyl salicylate.

Identification of Acetic Acid.—The aqueous alkaline liquid resulting from the saponification of the oil was acidified with dilute sulfuric acid and the mixture subjected to steam distillation. From the acid distillate a silver salt was prepared which, on ignition, yielded 65.7% metallic silver. Silver acetate contains 64 64% of silver.

Summary.

The chief constituent of this oil is α-pinene, a mixture of the *dextro* and *levo* forms. In addition, it contains salicylic acid and acetic acid, at least one alcohol, occurring both in the free state and combined as the acetate. The presence of borneol is quite probable.

ALABAMA POLYTECHNIC INSTITUTE,
AUBURN, ALA.

NOTES.

A Modified Kjeldahl Flask for Determining Soil Nitrogen.—Soil chemistry and soil bacteriology call for the determination of soil nitrogen. The nitrogen content of ordinary soil is small and the sample has to be correspondingly large. The fact that most directions call for the transfer of the solution between digestion and distillation shows that the ordinary Kjeldahl flask is not adapted to this determination. Some investigators do not make it a rule to transfer, but they sometimes are forced to, since with some types of soil, such violent bumping occurs that the flask breaks. The transfer is a nuisance, involving extra time and flasks, besides allowing a source of error.

The modified Kjeldahl flask represented in the accompanying sketch does away with the bumping, making the transfer unnecessary. This flask holds about 700 cc. It has the same proportions as the ordinary

Kjeldahl flask, except for its modified (more pointed) bottom. The
pointed bottom prevents the solid por-
tion of the contents from settling while
being heated. The silica and sludge
are thus kept in constant motion, ris-
ing straight up towards the surface of
the liquid and sliding back along the
sides of the flask. The hardest boiling
on the surface of the liquid is at the
center, and thus frothing is prevented
by the bubbles being broken against
the sides of the flask.
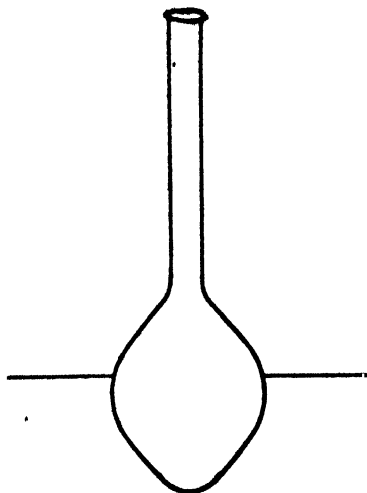
Over three hundred determinations
have been made in this laboratory with
this flask. Nitrogen has been deter-
mined in clays, loams, sands, peaty
sands, and peats. Neither bumping
nor troublesome frothing have oc-
curred in any case.   H. A. NOYES.

HORTICULTURAL CHEMISTRY LABORATORIES,
PURDUE EXPERIMENT STATION,
LAFAYETTE, INDIANA

Concerning the Quantitative Extraction of Diastases from Plant Tissues.—
"H. F. E. H." in a review of our recent article[1] on this subject, which
appears in a recent number of *The Analyst*,[2] states that "The authors
have overlooked the fact first shown by J. L. Baker and H. F. E. Hulton[3]
that the "Kjeldahl law of proportionality" does not strictly obtain up to
a production of 40% of maltose in the case of flour. There is no refer-
ence to the work of Brown and Morris,[4] and Ford and Guthrie,[5] who
showed that the diastatic activity of raw barley itself is greater than that
of any extract made from it. The great influence that amphoteric sub-
stances have upon the quantitative production of maltose from starch,
when flour, barley, etc., are employed, is ignored."

With reference to the first point, we recognize that Kjeldahl's "law of
proportionality" is not an absolute law in the sense that the reaction
velocity is absolutely unvarying up to the limits of unconverted starch to
which it was originally applied. This was shown by Brown and Glen-
dinning in the article to which we referred in our paper, much earlier than

[1] THIS JOURNAL, 36, 759–770 (1914)
[2] *Analyst*, 39, 160 (1914).
[3] *J. Soc. Chem. Ind.*, 27, 368 (1908).
[4] *J Chem. Soc.*, 63, 604 (1893).
[5] *J Inst. Brewing*, 14, 61 (1908).

by J. L. Baker and H. F. E. Hutton, whose work is mentioned by "H. F. E. H." But our own preliminary work bore out the statement of Brown and Glendinning that the curves of reaction velocity is sufficiently nearly rectilinear, up to the point of hydrolysis of 50% to 60% of the starch, "for all practical purposes of diastasimetry." We, therefore, did not hesitate to use the Kjeldahl "law of proportionality" as a basis for our study of the proposed method of extraction.

With regard to the supposed ignoring of the influence of substances in the material under examination upon the quantity of maltose produced from the starch in the sample, we may say that it was precisely in order to avoid this difficulty that we sought a method which would give an extract free from these disturbing substances. Our further investigations of the application of the proposed method to a study of the diastases of flour, which are now being prepared for publication, showed clearly that the accelerating effect of the extracts alone upon the conversion of starch to maltose is quite different from that of a dilute flour paste, exactly as indicated by the authorities cited by "H. F. E. H." Our investigations as to the causes of this phenomenon, while not yet complete, indicate that the difference is due to the presence in the flour paste of substances other than diastases which influence the rate of diastase action. This does not change in any way our conclusion that the diastases are quantitatively extracted at 0° by the proposed method. A discussion of this phenomenon belongs to the forthcoming paper, rather than to a description of the method of extraction, which was presented in our first paper. In the next paper, the work in question will not be "ignored."

R. W. THATCHER AND GEO. P. KOCH.

DIVISION OF AGRICULTURAL CHEMISTRY,
AGR EXPT. STATION, ST PAUL, MINN

NEW BOOKS.

A Laboratory Outline of Elementary Chemistry. ALEXANDER SMITH The Century Company, 1914

This outline is intended to accompany the author's new Text-book of Elementary Chemistry published by the same company during the summer. His position as Examiner in Chemistry of the College Entrance Board puts him in close touch with the teaching of Elementary Chemistry and two paragraphs from the preface give an idea as to the plan of the work:

"The apparatus has been made as simple and small in amount as possible. The list of chemicals has also been restricted to the least expensive materials and the smallest number of items. The indispensable experiments which are less simple, have been left for classroom demonstrations.

All the experiments, and the wording of the directions, have been tried under the author's supervision with young pupils, and have been altered until found satisfactory."

The book differs from the stereotyped forms in several important particulars. In the study of "Substances" the pupil is given pieces of white cotton cloth, of white mixed goods, and of woolen yarn instead of bits of copper, pieces of sulfur, nitric acid, etc. Incidentally, the ability to detect cotton and wool separately or in mixtures is developed. Measuring, weighing, density, changes in metals heated in air, follow, and then come studies in oxygen, hydrogen and water in quite the orthodox way. One exercise is devoted to hydrates and another to the determination of water in hydrates. (The old, misleading "Water of Crystallization" is not even mentioned. Let us hope that it, Sulphuretted Hydrogen and some others are on the road to oblivion.)

Why reactions proceed to equilibrium or to completion, ionization, normal and standard solutions, titrations, valence, give further practice in quantitative work not too difficult for beginners. Gram-molecular volume, colloids, starch and sugars, how soap cleanses, and tests for food compounds are new in the way of laboratory work for young pupils. The recognition of negative radicals, analysis of baking powder, hydrolysis, esters and soap-making, colloidal suspensions, hard water, film-cobalt chloride- and match tests for metallic elements, displacement of metals and the making of white lead are new features, or old topics treated in a new way.

The manual will make for itself some such place in elementary chemistry as his laboratory guide to accompany his first college text made in that field of the work.   C. M. WIRICK.

Collegiate Chemistry. By F W MARTIN, M S., PH.D   J. P. Bell Co Inc , Lynchburg, Va.   1914.   238 pp.   Price, $1.30

The author in this new text in General Chemistry has not introduced any strikingly new feature, and unfortunately leaves out some of the important old features. His work is based on the Periodic System and forms a very good introduction to Qualitative Chemistry. Although he particularly states in his preface that "it is probable that some who inspect it superficially may be misled by its size and simplicity of presentation into thinking that it is too brief in scope or too elementary in treatment to meet the needs of the college freshman," a very careful perusal leads one to the very conclusion to which the author objects. The sins of the book are more of omission than of commission. The brevity of the treatment is particularly apparent when the well known Frasch method for obtaining sulfur is not even mentioned—the lead chamber process for the manufacture of sulfuric acid is given only as a footnote. Catalytic agents are completely ignored, and while, in the prepara-

tion of oxygen, manganese dioxide is first used alone and then with potassium chlorate, the different role it plays in the two processes is not indicated. The only methods given for the preparation of ammonia are by treating ammonium chloride with lime and passing sparks through the gases hydrogen and nitrogen. Other illustrations could be given of the extremely brief treatment. Several chapters are devoted to the theories of chemistry, but there is no particular connection between the theories and the descriptive matter. The metallurgical processes given are not particularly good nor up to date. "Not-metal" is used in the place of the more euphonious "non-metal." Other unusual words such as acidigen and basidigen are used. The experiments embodied in the text are the usual standard ones. A good experimental illustration of the law of multiple proportions is given in the preparation of the two iodides of mercury. LILLIAN COHEN.

Collegiate Chemistry. Qualitative Analysis. By F W. MARTIN, M.S, PH.D. Professor of Chemistry, Randolph-Macon (Women's) College J. P Bell Co., Inc., Lynchburg, Va. 1914. pp. 257–321 Price, $1 00.

The Qualitative Analysis is Part V of Martin's Collegiate Chemistry. It is a satisfactory manual for qualitative analysis and with interpolations by the instructor could be used as a text-book. However, it does not possess any greater merit than most of the manuals on the market and not as much as some. LILLIAN COHEN.

A Text-book of Quantitative Chemical Analysis. By ALEXANDER CHARLES CUMMING AND SIDNEY ALEXANDER KAY. John Wiley & Sons, New York, 1913. pp. xi + 382.

In the ten parts of this book are considered (I) General Principles; (II) Volumetric Analysis; (III) Gravimetric Analysis; (IV) Colorimetric Methods; (V) Systematic Quantitative Analysis; (VI) The Analysis of Simple Ores and Alloys; (VII) Gas Analysis; (VIII) Water Analysis; (IX) Quantitative Analysis of Organic Substances; (X) The Determination of Molecular Weights. An Appendix contains data of various kinds. It can be seen that the scope of the book is large. The processes selected are representative and the manipulative descriptions of the typical exercises are unusually complete and satisfactory.

Many teachers will not concur with the authors in their decision to allow volumetric analysis to precede gravimetric analysis. The reader is frequently left in the dark as to the reasons why various precautions are necessary. Furthermore, no application is made of the modern theory of solution, even in such subjects as the solubility of precipitates, and neutralization in the presence of indicators.

Many detailed criticisms may be made: Under titration with permanganate in the presence of chlorides no mention is made of the useful-

ness of manganous salts in preventing error (p. 65). Oxalic acid is condemned as a standard reducing substance on the basis of effloresence (p. 67), whereas this phenomenon never occurs under any ordinary atmospheric conditions. Stannous chloride is stated to be applicable for iron reductions only when dichromate is used for oxidation (p. 76), yet this method of reduction is widely used in permanganate titrations with pre-precautions suitable for avoiding error due to chlorides. The diminution of the colloidal solubility of silver chloride by nitric acid is apparently confused with that of true solubility (p. 133). One is startled by the statement that cadmium is precipitated electrolytically upon the *anode* from cyanide solution (pp. 149 and 150). In the determination of the silica in an insoluble silicate, filtration of the second precipitate upon the same filter as the first is recommended.

The reviewer can see few points of superiority in this book over many other standard texts. G. P. BAXTER.

Photo-chemistry. By S E SHEPPARD, D Sc London Longmans, Green & Co, London and New York 1914 pp 446 (One of a Series of Text-Books of Physical Chemistry Edited by Sir William Ramsay, K C B , F R S) Price, $3 50

To those of us who have for a number of years been impatiently awaiting the promised appearance of a work on photo-chemistry, this latest addition to the Ramsay Series is especially welcome. One is struck at once by the appearance of thoroughness with which any one subject is discussed, and a closer study causes one to marvel at the amount of excellent material the author has succeeded in compressing into the 446 pages An especially desirable feature of the book, and one which the reviewer feels it impossible to over-emphasize because of the unusually widely separated literature of photo-chemistry, is its excellent bibliography, the collection and verification of which must have been a Herculean task.

One must commend the author for his excellent judgment in greatly condensing the historical development of photo-chemistry, in spite of the fact that the history of this branch of physical chemistry is one of unusual interest and inspiration. Following the six or seven pages of history we find about forty pages devoted to a thorough discussion of the principles involved in the measurement of light quantities; different light sources; standard light sources; and a brief, but comprehensive, description of the various devices used for the measurement of the intensity of light, including spectro-photometry.

Under the heading "Energetics of Radiation" the author takes up Kirchhoff's law; the Stefan-Boltzmann law; Wien's displacement law, Planck's law for the distribution of energy in the spectrum; the methods for determining temperature; the radiation scale of temperature; the mechanical equivalent of light, etc. The fourth chapter deals with

"Economic and Energetic Relations of Actual Light Sources," in which are discussed: the Hefner lamp; incandescent gas; incandescent electric lamps; the electric arc; various sources of the ultra-violet; sunlight; diffused daylight; and the distribution of energy in the spectrum of each.

The next seventy-one pages, constituting the fifth chapter, are devoted to a study of the absorption of light. The various factors influencing absorption are discussed in considerable detail, then the question of the absorption of solutions is considered at length. The remainder of the chapter is given over to a discussion, necessarily somewhat limited,[1] of the interesting question of the relationship between absorption and chemical constitution.

Chapters six and seven are devoted to "Statics and Kinetics of Photochemical Change" and "Dynamics of Photochemical Change." The former consists of an excellent discussion of the measurement of the rate of photochemical reactions and the application of the mass law, illustrated by numerous well-chosen examples. In the latter the author takes up the factors influencing photochemical equilibria; endo- and exo-actinic reactions; photochemical change in the elements; chemical actinometry; photochemical reactions in gases and vapors; photochemical induction and deduction; photochemical catalysis; and photo-sensitization.

Chapter eight is devoted largely to the photo-chemistry of the halogens; the silver compounds; and the interesting question of phototropy. This is followed by a chapter on "Radiant Matter and Photochemical Change," being mainly a discussion of the photo-electric effect. In Chapter ten there is an interesting presentation of what we know concerning the various luminescence phenomena, and a discussion of their theoretical significance. The last chapter in the book constitutes a very meager and rather disappointing discussion of organic photosynthesis, a subject which, though perhaps not so spectacular, is undoubtedly the most important of all.

Nearly one-half of the book is devoted to what many will undoubtedly call photo-physics rather than photo-chemistry, but in the opinion of the reviewer this is one of its strongest points. The author well says in his preface that the neglect of the bearing of photo-physical phenomena and laws and "too narrow a circumspection of its domain can only lead to further delay in the discrimination of a definite body of laws for this science."

The author is to be congratulated on giving us a presentation of real photo-chemistry, rather than a book lop-sided from the inclusion of too much photography. Dr. Sheppard has done much to dispel the popular

[1] This question has been quite fully discussed in a previous volume in this series. See Smiles," "The Relations between Chemical Constitution and Some Physical Properties."

illusion (unfortunately current even among chemists) that *photo-chemistry* and *photography* are synonymous. Any· such deluded person who will but look through this really excellent résumé of the field of photo-chemistry will never again be troubled by the vision of a camera rising before him whenever the word "photo-chemistry" is mentioned.

J. HOWARD MATHEWS.

Complex Ions in Aqueous Solutions. By ARTHUR JAQUES. · London: Longmans, Green & Co., 1914. 151 pp. Price, $1.35 net.

The first part of this monograph, approximately one-quarter of it, is devoted to a description of various general methods of investigating complex formation; namely, the chemical method, the ionic migration method, the distribution method, the solubility method, and the electrical potential method. In considering each method the principles are first presented, and then illustrated by applying them to actual experimental data. Properties of solutions, such as freezing-point lowering and vapor pressure lowering, which are a measure of the total number of mols of solute in the solution offer another important method for studying complexes. This method, though not classified as one of the general methods, is mentioned and illustrated by some of the examples given later in the book.

In the last part of the book these general methods are illustrated by examples, which also serve to give a review of some of the more important experimental work on complex ions in aqueous solutions. Unfortunately, no reference is made to investigations on the subject which have been published in this country.

M. S. SHERRILL.

Handbuch der Mineral Chemie. DOELTER, *et al.* Bd. III Nos. 3 and 4. (Bogen 21–40.) Dresden and Leipzig: Th. Steinkopff. Price, M. 6.50 each.

The mineral phosphates here treated are most of them rare and of little interest to chemists in general; indeed the examination of much of the contents of these two hefts has revealed comparatively little of a chemical nature.

There is some modern work on the synthesis of apalite, and some on the chemical behavior of turquoise which the mineral chemist should know, while the section on monazite and the extraction of the rare earths from it will appeal to a wider circle of readers.

The last pages of No. 4 in which the arsenic minerals are begun treat the polymorphic forms of this element, and those of arsenious oxide in a more complete manner than a strictly chemical treatise.

E. T. ALLEN.

The Source, Chemistry and Use of Food Products. By E. H. S. BAILEY, PH.D. Philadelphia: P. Blakiston's Son & Co., 1914. pp. xiv + 517. Price, $1.60 net

This is not intended as a reference book for experts or specialists, but

as a convenient manual for the use of students in colleges or high schools, and especially for those who are taking courses in dietetics or household economics. An unusually large amount of practical information, gleaned largely from original sources, is condensed in the book and the presentation is such that the student should be able to grasp readily the essential points. There is unquestionably a place for such a book and the author has succeeded in compiling something which is really needed.

Dogmatic statements on some controverted questions have been pretty well avoided. A few paragraphs, here and there, seem to the reviewer, however, somewhat wide of the mark, and in future editions should be modified or omitted. The author has occasionally gone out of his way, for example on page 295, in making statements which do not well accord with the facts. In discussing the use of preservatives in a well-known tomato product, the author discloses a somewhat uncertain prejudice, not in keeping with the scientific accuracy which should ever hold in a book for students.

While many foods, because of their limited use in this country, are but briefly discussed, other sections are much longer and full enough to form very interesting reading. The chapters on sugars and bread are examples of quite satisfactory treatment. Numerous illustrations add much to the practical value of the book, which, on the whole, can be cordially recommended to the readers for whom it is intended.   J. H. LONG.

A Manual of Bacteriology for Agricultural and General Science Students. By HOWARD S. REED   Ginn & Co   1914   Price, $1.25

This volume consists essentially of a well-selected series of experiments designed to familiarize the student with principles underlying the activities of bacteria, yeasts, and molds. The majority of these experiments are devoted to bacteriological technique and the role of bacteria in nature; nevertheless, considerable space is occupied by a consideration of various fungi, particularly yeasts and molds. The scope of the volume, therefore, is greater than the title would indicate.

The viewpoint of this manual is essentially chemical. Attention is directed continually toward the nature and extent of microbic activity; but little space is devoted to their morphology and botanical identification. This omission of morphological details, however, is of little moment, for the practical importance of microbes in the last analysis centers around the results they accomplish rather than what they are. The essential morphological features can be readily supplied by collateral reading: a selected list of texts is appended for this purpose.

The arrangement of the book might be unified somewhat without seriously disturbing the sequence of the text by uniting Sections II and V, both of which deal essentially with the preparation of general and special media for the cultivation of microörganisms. Similarly, Experiments

27 and 28 of Section VI might well be contained in Section VIII, which is devoted to the isolation of a pure culture. It might be advantageous from the viewpoint of the student, furthermore, to amplify Section VIII by the addition of experiments illustrating the general methods of obtaining pure cultures of microörganisms from their mixtures.

Section XV, "Bacterial Disease in Man and Animals," is not impressive. The subject is inherently far beyond the scope of a volume the size of this manual, and it might be profitably omitted entirely, or, at most, dismissed with the most general statement.

Sections XI and XIII, dealing, respectively, with bacteria of water and sewage, and bacteria of milk, are worthy of special mention. Section XII, relating to the bacteria of the soil, taken together with the information contained in the appendix on the sterilization of soil, is excellent.

The appendix contains directions for the accurate determination of various products of microbic growth.

The student who successfully completes the experiments outlined in this manual should be well grounded in general mycology.

<div style="text-align:right">ARTHUR I. KENDALL.</div>

A Text-book of Physiological Chemistry. By OLOF HAMMARSTEN with the collaboration of S G. HEDIN. Authorized translation by John A. Mandel, from the enlarged and revised 8th German edition New York. John Wiley & Sons. pp. viii + 1026. 1914. Price, $4.00 net.

This well-known work here appears in the 7th American edition. The preface of the 6th edition was dated April, 1911, while in the new edition the date is June, 1914, following closely the corresponding German dates. Former editions have been reviewed at length in the JOURNAL. The translater calls attention to the fact that the last German edition, from which this is taken, was revised by the author himself, who is now in his 73rd year. Every worker in the field of Physiological Chemistry will doubtless join heartily in the wish that the pioneer investigator and painstaking compiler may live in vigor to bring out many future editions of a hand-book which has long been a necessity in the library of the biochemical student.

This new edition shows a considerable number of changes to correspond to the rapid advances in the science. By a rearrangement of the matter the number of chapters has been reduced from eighteen to seventeen, and practically every chapter has received additions. In Chapter I, dealing with general physico-chemical relations of physiologically important bodies, the sections on osmotic pressure, colloids, catalysis, enzymes, and ions and salt action, the revision has brought important discoveries and theories down to date. In no field of physiological chemistry has the development been more rapid than just here and the fact is fittingly regarded in the compilation. For example, even some of the

latest determinations of the reaction of the blood by gas chain methods have received attention.

Notable changes have been made in other chapters, and especially in the work on the blood and the urine. The preliminary discussion on oxidation processes in the body, which in earlier editions came in the first chapter, now appears in the sixteenth chapter under respiration and oxidation. In some chapters the changes appear to be slight, for example, in the discussions of the carbohydrates and the animal fats and phosphatides.

The work of the translator must be again commended, as well as that of the publishers in keeping up the excellent appearance of the book.

J. H. LONG.

Preservatives and Other Chemicals in Foods. By OTTO FOLIN, PH D Hamilton Kuhn, Professor of Biological Chemistry, Harvard University Cambridge: Harvard University Press, 1914. 60 pp. Price, $0 50

This little volume is the outgrowth of one of the Harvard health talks by Dr. Folin. It is one of the best and fairest presentations of the question of chemical preservatives in foods that has thus far been published. Dr. Folin does not wholly condemn the use of preservatives in food products, but condemns their use as a substitute for sanitation or of the use of any of the more harmful ones.

The author says:

"Unfortunately, the application of these new methods for preserving food was not left where it belonged, with the critical and disinterested scientific investigators, but was seized upon by alert men whose chief interest was of the pecuniary kind. The outcome might have been foreseen. * * *

"By means of greater liberality with the antiseptics which are cheap, the enterprising manufacturer also succeeded in preparing food products for the market from materials already so decayed as to be unsalable. * * *

"In the absence of specific and adequate evidence to the contrary, it follows practically as a matter of course that chemicals which are effective in killing or preventing the development of bacteria must be injurious to the more highly organized and more sensitive living cells which go to make up the human body. * * * *

"Among all the preservatives of recent origin there is probably no one more likely to prove practically harmless to human beings than benzoic acid and benzoates.

"It is known that while certain chemicals may be taken in substantial quantities for a month or a year without producing demonstrably injurious effects, nevertheless, the continued use of the same substance, even in small quantities, will eventually undermine the health.

"It is perhaps not superfluous to state that the approval of a limited

use of benzoic acid or sodium benzoate for the preservation of good, but perishable food materials, does not imply approval of similar preservation of decayed materials; or of materials which are regularly consumed in large quantities, as for example milk; or, of foods which do not need any chemical preservatives."

"The substitution of benzoic acid for cleanliness in the preparation of food is doubtless a real and practical temptation to manufacturers of cheap foods, however much they may be disposed to deny it."

"It is, however, extremely difficult—in food almost impossible—to determine experimentally, in a short time, with any degree of certainty, whether a comparatively mild chemical is or is not injurious to health."

Dr. Folin does not hesitate to condemn the bleaching of flour. He says:

"The addition of dangerous chemicals to food products for no other purpose than to hide inferiority is a practice which, from the standpoint of the consumer, has nothing to recommend it. Take for example the notorious case of bleached flour."

He points out that the owners of the patent have worked for years and "the reward for their success was contributed by the consumers of the bleached flour at the rate of 50 cents to $1.00 extra per barrel."

"We are, in my judgment, bound to take the position that any substance known as a poison must be assumed to be injurious to health, even when taken in the smallest doses, unless we have definite and specific reasons for believing it fails to have *any* effect when the dose is minute. * * * In the case of most dangerous chemicals it is, I think, neither safe or sound public policy to assume that they may be made ingredients of our daily food even though the quantities used are small when compared with doses capable of producing demonstrable results. So long as failing health before old age is as common as it is we cannot afford to extend the benefits of reasonable doubts to any poisonous or deleterious ingredients added to our food. * * * In the interests of the public it should be enough to show that adulterated foods contain added poisonous or deleterious ingredients, and to insist that the presence of such admittedly injurious substances of necessity renders the product containing them injurious to health."

The author thinks that the courts may safely interpret the phrase "may render such article injurious to health" as throwing the burden of proof on the manufacturers of foods containing added chemicals.

This little volume may be read with much profit by all who are interested in food products as a sane presentation of facts sifted from the mass of controversial material forced upon the public during the past few years.

E. F. LADD.

Author Index to Volume XXXVI, 1914.

PROCEEDINGS.

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GENERAL SOCIETY MINUTES AND REPORTS.

On November 21, a nominating ballot was sent to all members of the Society as required under the Constitution, the following being the nominees of the membership sent to the Council for election:

President: T. W. Richards, C. H. Herty, L. H. Baekeland, W. E. Henderson.

Councilors-at-Large: C. H. Herty, Julius Stieglitz, L. H. Baekeland, W. L. Dudley, H. G. Byers, E G. Love, S. L. Bigelow, R. H. McKee.

The ballot was counted by a committee consisting of C. L. Parsons, Percy S Walker and S. S. Voorhees, assisted by seven other members of the Society.

The result of the election by the Council will be found in the Council minutes.

Report of the Secretary of the American Chemical Society for the Year 1913.

The rate of growth of the American Chemical Society, during the year 1913, has shown some falling off from that of 1912, when special interest was awakened among chemists of the country on account of the meeting of the Eighth International Congress of Applied Chemistry. However, the Society has maintained a healthy growth of 454 members for the year. The membership of the Society at the end of 1912 was 6,219. It is now 6,673. Statistics follow:

Honorary members. . . .	14
Life members . . .	13
Corporation members	64
Members	. 6 582

Total.	6,673

During the year the deaths of the following members were reported to the Secretary: E. S. Renwick, New York City; J. B. Smith, Williamsburg, Mass.; Belle F. Schulman, Brooklyn, N. Y.; R. C. Burris, Carnegie, Pa.; F. A. Blaicher, St. Louis, Mo.; E. F. Billings, Boston, Mass.; T. P. Cook, New York City; E. E. Dunlap, Philadelphia, Pa ; O. C. Johnson, Ann Arbor, Mich.; Dr. Fred'k Schniewind, New York City; T. E. Senior, Boston, Mass.; M. McMurtrie, New York City; L. D. Gilbert, St. Louis, Mo.; J. R. Mitchell, Ft. Worth, Texas; O. T. Klooz, Chicago, Ill.; W. F. Jones, Chelsea, Mass.; W. J. Evans, New York City; E. A. Byrne, Washington, D. C.; T. E. Smith, Weehawken, N. J.; C. J. Lawler, Brooklyn, N. Y.; H. H. Sutro, Jersey City, N. J.; O. W. Knight, Portland, Maine; Arthur Edgar, White Haven, Pa.; Louis Gilbert, Santa Rosa, Cal.

The number of members not in arrears registered in the Local Sections on December 1, 1912, was 4,674; the number on December 1, 1913, was 5,069. The number in each Section for 1912 and 1913 is noted below:

Local section.	Number of paid members, 1912.	Number of paid members, 1913.	Cash retained from balance, 1912.	Total Dr. account, 1913.
Alabama	...	31	...	25.00
California	145	174	...	145.00
Chicago	416	437	...	312.00
Cincinnati	102	102	23.82	123.82
Cleveland	144	166	21.87	121.87
Columbus	51	47	3.69	53.69
Connecticut Valley	57	62	...	50.00
Cornell	46	52	...	50.00
Detroit	65	64	40.15	40.15
Eastern New York	58	63	17.23	67.23
Georgia	42	59	...	50.00
Indiana	104	100	...	130.00
Iowa	52	52	16.88	16.88
Kansas City	83	80	7.98	103.75
Lehigh Valley	48	59	16.37	66.37
Lexington	22	25	...	25 00
Louisiana	32	35	...	40.00
Louisville	19	18	...	...
Maine	37	41	0.05	25.05
Milwaukee	51	52	...	75.00
Minnesota	86	83	69.17	69.17
Nashville	23	21	15.61	15.61
Nebraska	33	29	...	...
New Haven	52	58	3.35	40.00
New York	906	1,006	14.95	514.95
North Carolina	26	38	15.00	40.00
Northeastern	449	478	8.86	258.86
Northern-Intermountain	19	16	...	...
Oregon	27	29	..	50.00
Philadelphia	296	297	36.44	186.44
Pittsburgh	204	230	41.36	191.36
Puget Sound	39	45	...	50.00
Rhode Island	51	57	21.41	46.41
Rochester	29	38	...	50.00
St. Louis	76	83	...	90.00
Southern California	79	84	...	75.00
Syracuse	74	77	...	92.50
University of Illinois	80	88	20.38	60.38
University of Michigan	34	35	20.66	45.66
University of Missouri	17	18	9.70	9.70
Washington, D. C.	351	365	...	263.25
Western New York	79	91	...	98.75
Wisconsin	70	84	3.46	87.50
	4,674	5,069	$428.39	$3,856.35

The table gives a summary of the sectional accounts for the year, shows the number of members in each Section for the present year and during 1912, the funds held over from 1912 account, and the total funds (which include the balances) charged to the 1913 account

During the fiscal year, December 1, 1912, to December 1, 1913, the Secretary has made collections to the amount of $71,825 89, divided as follows

Membership dues	$62,158 00
Subscriptions	4,998 00
Back numbers	2,417 95
Postage	951 09
Reprints	681 85
Exchange	19 79
Interest	399 21
Life membership	200 00

$71,825 89

This amount was duly transmitted to the Treasurer of the Society

The sales of back numbers during the past year has increased rather than diminished as had been expected   This is due to the fact that efforts have been continually made to induce libraries to pu hase complete sets, and owing to the fact that the subscription list is continually enlarging, and purchasers desire early numbers as well

Several complete sets have been sold to foreign and domestic libraries and several incomplete sets have been completed by the purchase of odd volumes where they could not be furnished from stock   The stock has been kept in good condition by the purchase of numbers needed to complete full volumes and by reprinting three small numbers issued in the early years of the Society   A few complete sets are still available for sale.

Back numbers are mailed direct from Easton, Pennsylvania, on orders sent out through the Secretary's Office   The following is a summary of the back numbers sent out by the Secretary during the year, together with the present stock of Journals and the condition of the Society's mailing lists

Copies of the Society's publications sent out from December 1, 1912, to December 1, 1913, aside from mailing lists	26 438
Copies of the *Jour Amer Chem Soc* in stock	25,483
Copies of the *Chemical Abstracts* in stock	17,994
Copies of the *Jour Ind & Eng Chem* in stock	7,522
Copies of the General Index, Vols 1–20, *J A C S* in stock	450
Copies of the Anniversary Number in stock	267
Mailing list for both Journals and *Chemical Abstracts*	6,212
Mailing list for *Chemical Abstracts* only	187
Mailing list for *Jour Amer Chem Soc* only	443
Mailing list for *Jour Ind & Eng Chem* only	361

The Secretary wishes to express his appreciation to the members of the Society for their continued assistance and loyal support of his efforts to

administer the duties of his office, without which little could have been accomplished. Respectfully submitted,

CHARLES L. PARSONS, *Secretary*.

Report of the Editor of the Journal of the American Chemical Society for the Year 1913.

During the years 1912 and 1913 papers and book reviews have been published as follows:

	Pages.		Number of papers.	
	1912	1913.	1912.	1913.
Proceedings...........................	132	114	...	...
Physical and Inorganic......	948	1029	126	107
Organic and Biological.............	736	818	88	111
Book Reviews..............	61	75	69	85

During the past year 13 papers have been referred to the Editor of the *Journal of Industrial and Engineering Chemistry* as more suitable for publication in that journal than in the *Journal of the American Chemical Society*. Fifty papers have been returned to the authors for revision or because they were not considered suitable for publication. Nineteen papers have been published after revision.

The Board of Editors has recently decided by a decisive, though not unanimous, vote, to return to the conventional spelling in the use of the final "e" in such words as medicine, alkaline, urine, etc. The following reasons have led to this decision:

1. The opposition of a number of our contributors, including several who have given us some of our most important papers.

2. Because in such words as crystalline, alkaline and some others, two pronunciations are in good usage, the long "i" being used in England, and in some parts of the United States, while the short "i" is, on the whole, in common use in America. In such a case one is in doubt whether to use the "e" or to drop it.

3. About thirty years ago the Chemical Society, London, adopted the rule that the names of basic substances, such as aniline and strychnine, should be spelled with the "e," while names of substances which are not bases, as paraffin, and stearin, should drop the "e." This rule has come into universal use in England, and has always been used both in our Journal and in the *American Chemical Journal*. Because of this rule our rule No. 6. makes an exception in the case of chemical names. Such an exception is illogical, but I should be very sorry indeed to drop the "e" from such words as aniline and glycine, on account of the English usage, as well as because of the useful distinction which is made by retaining it.

4. The dropping of the final "e" would logically compel us to drop it in

such a word as surplice, but this seems impossible, unless we spell the word surplis.

Two members of the Board of Editors, Professors A. A. Noyes and H. P. Talbot, have recently withdrawn from the work of the Board, at their own earnest request. Each of these men has given to the Society a very large amount of unselfish work and their careful criticism of papers has aided very greatly in maintaining a high standard of excellence for our Journal. We are very fortunate in securing the addition of Professor W. Lash Miller, of Toronto, to the Board.

Last spring President Remsen told me that he would be willing to have the American Chemical Society continue the publication of the *American Chemical Journal* after the completion of the fiftieth volume of that journal, which closed with the December number of 1913, provided some satisfactory arrangement could be made. Various methods of consolidation were discussed during the summer and a scheme which involved also the *Journal of Physical Chemistry* was brought informally before the Council by correspondence. At the Rochester meeting it was voted by the Council that the *Americal Chemical Journal* should be incorporated with the *Journal of the American Chemical Society*, provided such an arrangement was satisfactory to President Remsen and the consolidation could be made without separate pagination.

After this action had been taken, a number of members of the Organic Division expressed a strong desire that the *American Chemical Journal* should be continued under the auspices of our Society as a separate journal and made our organ for the publication of papers in organic and biological chemistry. A postal card vote among the members of the Organic Division gave the result that 88% of those voting were in favor of separate publication for the *American Chemical Journal*. After presentation of the matter to the Board of Directors and Council, however, it has been decided by both bodies that separate publication is inadvisable at the present time. The opposition is based chiefly on the opinion of the Board of Directors that it would be financially impossible to furnish four journals to the members of our Society without an increase in the dues. In accordance with the action of the Directors and Council, the *American Chemical Journal* will be incorporated with our Journal as an integral part, beginning with January, 1914, and this incorporation will be indicated by a statement on the cover of the Journal.   W. A. Noyes, *Editor*.

Report of the Editor of Chemical Abstracts for the Year 1913.

In order to keep *Chemical Abstracts* from exceeding its appropriation in 1913, it was found, early in the year, that it would be necessary to make the abstracts shorter than ever before. The growth of the literature has been such that 3,285 more abstracts than were printed last year,

required publication. In spite of the elimination of several hundred abstracts of doubtful value, the limit of 170 pages per issue which our budget allowed, has crowded the average abstract into 0.173 page. The history of the reduction in length of abstracts is best illustrated as follows:

Year.	Pages (blanks omitted).	No. of abstracts.	Length of abstracts.	Pages patents.	No. of patents.	Length of patent.
1907	2584.4	7,975	0.324	462.0	not	...
1908	2928.5	10,835	0.270	355.3	counted	...
1909	2565.3	11,455	0.224	365.8	3806	0.096
1910	2894.9	13,006	0.223	387.0	3754	0.103
1911	3260.3	15,892	0.205	542.8	5014	0.108
1912	2888.6	15,740	0.183	537.5	6919	0.077
1913	3292.5	19,025	0.173	576.4	6946	0.083

The main and important cause of this steady reduction is of course the increasing volume of literature abstracted. To the 598 journals on our list in 1912, 35 have been added and some of the new ones are very valuable. From the table below it may be seen that the balance of departments has been fairly well preserved. The large increases in numbers of abstracts have been in the larger departments and the largest reductions in length of abstracts have been so distributed. During 1914 our policy will be to exclude more than ever the material which is hardly chemical. On the other hand, we had hoped to increase our foreign patent department; to make foreign patents approximately complete, at least 2000 more should be printed. How this can be done and the 170-page limit be maintained is not yet clear.

In order to save expense in printing, the policy was adopted this year to give the first authors name only, in the parenthesis after the entry in the Subject Index. For the same reason, in 1914, the black face titles of abstracts will be printed all lower case.

W. H. Ross has assumed the work of Herman Schlundt in Radioactivity; in Mineralogical and Geological Chemistry R. C. Wells resigned in favor of Edgar T. Wherry, and in Soils and Fertilizers M. X. Sullivan is assisting F. P. Veitch. For the faithful service of the older men the Society is deeply indebted and for the enthusiasm and energy of the new assistants the editors are truly grateful.

By the faithful work of the entire office force and the coöperation of the assistant editors, abstractors and printers, the Annual Index, which is by far the largest of its kind in the world (containing 82,000 entries), will this year be in print in December and at the same time include the maximum amount possible of the year's chemical work.

The summary by departments is as follows:

	No pages.		No abstracts
Apparatus	41	9	365
General and Physical Chemistry	350	2	1807
Radioactivity	65	4	333
Electrochemistry	67	2	416
Photography	14	6	101
Inorganic Chemistry	90	6	417
Analytical Chemistry	109	8	551
Mineralogical and Geological Chemistry	67	3	496
Metallurgy and Metallography	109	3	808
Organic Chemistry	597	2	1651
Biological Chemistry	841	3	5477
Foods	109	9	716
Water, Sewage and Sanitation	80	1	691
Soils and Fertilizers	76	6	578
Fermented and Distilled Liquors	44	3	286
Pharmaceutical Chemistry	111	9	825
Acids, Alkalies Salts and Sundries	15	5	191
Glass and Ceramics	43	9	386
Cement and Other Building Materials	50	2	360
Fuels, Gas and Coke	59	0	500
Petroleum, Asphalt, Coal Tar and Wood Products	51	1	322
Cellulose and Paper	30	9	176
Explosives	37	7	217
Dyes and Textil Chemistry	50	1	267
Pigments, Varnishes, Resins and India Rubber	65	8	418
Fats, Fatty Oils and Soaps	32	0	223
Sugar, Starch and Gums	49	2	296
Leather and Glue	29	5	151
Total, not including patents	3,292	5	19,025
Patents	576	4	6,946
	3,868	9	25,971
Headings, blanks, cross references, book titles	227	1	

4,096 0

Respectfully submitted,

AUSTIN M. PATTERSON, *Editor*.

Report of the Editor of the Journal of Industrial and Engineering Chemistry for the Year 1913.

The *Journal of Industrial and Engineering Chemistry* published 1052 pages of reading matter, including index, and 604 pages of advertisements in the 1913 volume. Of a total of over 850 articles published, more than 300 were direct contributions by authors The following table gives a summary of the work of the *Industrial Journal* for the past three years:

	1911.	1912.	1913.
Pages in editorial section....................	970	946	1052
Pages in advertising section.................	158	494	604
Total pages printed...................... ...	1128	1440	1656
Editorials..... ...., ...	30	19	28
Original papers...	140	160	179
Addresses	22	37	57
Laboratory and Plant articles............	28	55	43
Book Reviews......	36	53	52
Patents...	..	.	172

The additional material in the 1913 volume is made up of Current Industrial News, Scientific Society Reports, Notes, Abstracts from Government Reports, and general correspondence.

The Associate Editors have been of the greatest possible assistance, both in passing on the value of the papers submitted and in working in the interests of the Journal. The full responsibility of determining the quality of the original contributions submitted in their respective fields has been placed upon them, and their decision has been final. The quality of the original matter published in the Journal will always depend largely upon the judgment of the Associate Editors, and it is essential that this Board be held in its present high state of efficiency.

Authors are again urged to exercise greater care in the preparation of their papers. Figures, formulas and references should be verified on the copy before it is sent in and not on the proof. Proof changes by the authors or editors are made at the expense of the Society. Authors are also urged to condense their material. Illustrations are advised wherever possible, as they are preferable to lengthy descriptions and are usually easier to understand.

During the year, the contract for printing the *Industrial Journal* has been entirely revised, with a view to establishing a more equitable division of the costs of production of the various items, and thereby enable us to compile some intelligent cost figures and also to indicate possible directions for economies.

The *Industrial Journal*, with its constantly growing circulation, both in this country and abroad, will continue to attract advertisers in increasing numbers.

The editors are improving every effort to improve and strengthen the editorial section of the *Industrial Journal*, and in this, as in all other features of its development, we need the coöperation of every member of the American Chemical Society.   ·M. C. WHITAKER, *Editor.*

Treasurer's Report.

From interest

Farmers Loan & Trust Co	96	65
Certificate of deposit	300	00
1st National Bank, Yonkers	24	59

From interest on investments

Atlas Portland Cement Bonds	120	00

From interest on special funds

Special investment fund	570	00
Life membership fund	135	00
	92,973	64

	$97 030 85	
Morris Loeb Endowment Fund	$25,000 00	

ASSETS

Special Investment Fund

$2000 3$1/2$% N Y City gold bonds due 1915	$1 950 00	
$10 000 U S Steel Corp gold bonds 1963	10 075 00	
		$12,025 00
Atlas Portland Cement Co bonds 6%		2,040 00

Life Membership Fund

$1,000, 3$1/2$% N Y City gold bonds due 1928	$895 00	
$2,000, 6% Mutual Telegraph Co bonds due 1941	2 128 33	
Emigrant Savings Bank	388 22	
		$3,411 55
Balance Farmers Loan & Trust Co	$5,413 25	
Balance First National, Yonkers	2,901 73	
		8,314 98

	$25 891 53

LIABILITIES

Life Membership Fund	388 22
Excess assets over liabilities	$25,503 31
	$25 891 53

DISBURSEMENTS

Journal, Editor's salary

Journal, Editor's salary	$1,000 00	
Assistance to Editor	237 00	
Expense	129 09	
Printing Editorial	9,034 35	
Printing, Advertisements	334 59	
Reprints	731 03	
		$11,466 06

Chemical Abstracts, Editor's Salary	$500 00	
First Associate Editor	1,700 00	
Second Associate Editor	1,200 00	
Assistance to Editor	2,232 99	
Expense	628 78	
Abstractors	8,147 22	
Printing, Editorial	22,381 32	
Printing, Advertisements	468 32	
		$37,258 64

Jour. Ind. & Eng. Chem., Editor's Salary......................... $1,000.00
    Assistant Editor....................................... 1,337.50
    Expense.. 952.34
    Clerical... 1,032.00
    Reprints... 1,489.42
    Printing, Editorial................................ 11,318.26
    Printing, Advertisements........................... 4,704.10
               ————— $21,833.62
Advertising Commission, H. F. Mack................. .... 441.09
    Salary, Advertising Manager.................... . .. $3,635.03
    Expense.. ..... 513.15
               ————— $4,148.18
Secretary's Office, Clerical............................ $2,218.32
    Expense.. 1,532.69
    Commission on collections....................... .... 3,591.29
               ————— $7,342.30
Treasurer's Office Salary.............................. 300 00
    Expense.. 400.00
               ————— $ 700.00
General Meetings....... .... 654.51
Local Sections.. . 3,406.31
Back Numbers... . 689.37
Incidentals... 308.69
Committee on business organization...................... 232.10

                                            $88,480.87
Life Membership Fund................................... 235.00
Balance on hand, Dec. 1, 1913.......................... 8,314.98

                                            $97,030.85
                     A. P. HALLOCK, *Treas.*

BOARD DIRECTORS.

The Directors of the American Chemical Society met at the Chemists' Club, New York City, Monday, November 24th, at eight o'clock, P. M., with Messrs. Little, Love, Hallock, Smith, Bigelow, Bogert, Parker, and Parsons, present.

It was voted to accept the invitation of the Cincinnati Section and the Cincinnati Chamber of Commerce to hold the Spring meeting of the Society in Cincinnati, near the middle of April, the exact date to be settled by the President and Secretary.

It was voted that the date of the Fall meeting, to be held in Montreal, shall be September 8–11.

It was voted that 200 copies of the January *Journal of Industrial and Engineering Chemistry* be donated to the Eighth International Congress of Applied Chemistry, and that the cost of these extra 200 copies be charged to the account of Incidentals.

It was voted that the recommendation of Editor Whitaker that re-

prints without covers be standardized for the *Journal of Industrial and Engineering Chemistry* be approved

It was voted that reprints furnished to authors above the 50, now given gratis, be supplied to them at a price as near to the actual cost of printing and distributing as possible.

It was voted that the life membership fund, together with all income from that fund up to January 1, 1914, be capitalized as a life membership fund and that thereafter the income from this fund be used first to pay the dues of the living life members, and that any balance be set aside for research grants

It was voted that the Secretary and Treasurer transfer annually from the income of the life membership fund to the general fund of the Society an amount equivalent to the dues of the life members

It was voted that the communication of E J Gibling, of October 25th, in regard to the charges for classified advertisements and the question of the number of insertions permitted to paid members of the Society seeking employment be referred to the Advertising Committee with power.

In response to the request of Dr Charles Baskerville, Chairman of the Committee on Business Methods, for funds to defray the expenses of the members of that committee in attendance at a meeting to be held in New York, it was voted that a sum, not to exceed $250, be appropriated from funds in the treasury of the Society, not otherwise appropriated, to defray the expenses of the committee, provided such expenditures result in the attendance at such meeting of a working majority of the committee.

It was voted that T J. Parker be authorized to represent the American Chemical Society at a meeting to be held before the Surrogate of the County of New York at the Surrogate's office, on the 31st of December, 1913, in regard to any business covering the interests of the American Chemical Society in the estate of the late Morris Loeb

The following budget was then adopted for 1914

<div align="center">

BUDGET FOR 1914.

RECEIPTS
</div>

Secretary's office	$72,000
Advertisements	20,000
Interest	1,000
Total	**$93,000**

<div align="center">EXPENDITURES</div>

Journal American Chemical Society

Editor's salary	$ 1,000
Expenses, including reviews	600
Printing, including reprints	14,400
Total	**$16,000**

Chemical Abstracts:

Editor's salary...	500
First assistant editor's salary...............................	2,000
Second assistant editor's salary............................	1,400
Clerical assistance..	2,550
Expenses...	600
Abstractors and department heads..........................	8,450
Printing, including index..................................	24,500
Total..	$40,000

Journal of Industrial and Engineering Chemistry:

Editor's salary...	1,000
Assistant editors' salaries...............................	2,590
Clerical and office expenses..............................	1,836
Printing, editorial.......................................	11,500
Printing, advertisements..................................	6,600
Total....................................	$23,526
Advertising manager......................................	$ 5,000

Secretary's office:

Collection commissions....................................	3,500
Expense..	1,600
Clerical..	2,600

Treasurer's office:

Salary...	300
Expense..	400
President's office...	50
Local sections...	3,800
General meetings..	600
Incidentals...	800
Back numbers...	600
Grand total...................................	$98,776

It was voted that the collection commissions of the Secretary's office shall not exceed the annual sum of $3,500.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary.*

COUNCIL.

President Little has made the following appointments:

Officers of the Section of Water, Sewage and Sanitation, Edward Bartow, Chairman, and H. P. Corson, Secretary.

Delegates to the meeting of the American Road Builders' Association, held in Philadelphia, December 9, 10, 11 and 12th, Clifford Richardson, Charles L. Reese and Provost Hubbard.

On November 19, a nominating ballot for Directors was sent to the Council, the following being the four leading nominees which, according to the Constitution, are sent to the Council again for the selection of two:

M. T. Bogert, T. J. Parker, H. P. Talbot, A. D. Little.

This ballot was counted by a committee consisting of C. L. Parsons, Percy S. Walker, and S. S. Voorhees.

On November 28, these nominees were sent to the members of the Council and also the nominees for President and Councilors-at-Large, as selected by the membership. (See General Society minutes.) As a result of this ballot, the following officers were elected:

President, T. W. Richards for the term January 1, 1914, to January 1, 1915.

Directors, M. T. Bogert and A. D. Little for the term January 1, 1914, to January 1, 1917.

Councilors-at-Large, C. H. Herty, Julius Stieglitz, L. H. Baekeland, W. L. Dudley for the term January 1, 1914, to January 1, 1917.

This ballot was counted by a committee consisting of C. L. Parsons, Gilbert Rigg and J. D. Davis.

On November 21, 1913, the following communication was sent to the Council:

<div align="center">AMERICAN CHEMICAL SOCIETY.</div>

<div align="right">WASHINGTON, D. C.
BOX 505,</div>

Council of the American Chemical Society.   November 21, 1913.

GENTLEMEN.

I am sending you herewith a communication from Dr. W A. Noyes; President Little's reply thereto; and the comments of each Director thereon, the last of which reached me only this morning.

While the Directors feel that the matter has been fully covered and the majority doubt the necessity or expediency of this communication, President Little has deemed it wise to direct me to send it to the Council to meet Dr. Noyes' wishes in the matter, and to leave no doubt as to the advice which the whole body would have given, had they been assembled in Rochester.

For your information the following is included:

At the Rochester meeting th· following votes of the Directors were spread on the minutes:

"It was voted that whereas Dr. W. A. Noyes has submitted to the Directors a scheme for the consolidation of the *American Chemical Journal* and the *Journal of Physical Chemistry* with the *Journal of the American Chemical Society*, the Directors are at present of the opinion that the only scheme of consolidation practicable is one whereby the *Journal of the American Chemical Society* keeps its full name and volume numbers, to which may be added, in smaller type, for a limited number of years, the words: 'with which has been incorporated the *American Chemical Journal* and the *Journal of Physical Chemistry*,' one or both, without continuing the volume number of either journal."

This vote was transmitted to the Council and the advice of the Council asked. The Council voted on September 8th as follows:

"* * * It is the sense of the meeting that, with President Remsen's consent, the *American Chemical Journal* be incorporated with the *Journal of the American Chemical Society* provided it can be done under the title of the *Journal of the American Chemical Society*, and without separate pagination."

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The day after the Council meeting, Dr. Noyes appeared with Dr. John H. Long and Dr. Treat B. Johnson, and argued before the Directors in favor of continuing the *American Chemical Journal.* The Directors then voted:

"That they are in entire accord with the advice of the Council as recorded in the Council minutes of September 8, and they are not in favor of continuing, at the expense of the Society the *American Chemical Journal* as a separate publication or of combining it with the *Journal of the American Chemical Society,* with separate pagination. It was voted that, if President Remsen should favor placing the words 'with which has been incorporated the American Chemical Journal, founded by Ira Remsen,' in smaller type, beneath the title of the *Journal of the American Chemical Society,* during his life, the President and Secretary are authorized to agree to such incorporation, provided the *American Chemical Journal* is discontinued."

Following the meeting the Secretary entered into communication with President Remsen, and a definite agreement was arrived at according to the vote of the Directors, and confirmed by President Remsen and President Little, this agreement being that the *American Chemical Journal* shall be discontinued with the December number, and that the words "with which has been incorporated the American Chemical Journal, founded by Ira Remsen," shall be placed during the lifetime of President Remsen in smaller type, under the title of the *Journal of the American Chemical Society.* This agreement will be found announced in the November Journals of the Society.

Kindly cut off the slip at the end of this communication and mail it to me in the enclosed ballot envelope to reach me on or before December 12th.

Very truly yours,
CHARLES L. PARSONS, *Secretary.*

To the Council of the American Chemical Society.   Urbana, Ill , October 25, 1913.
DEAR SIRS:

At the Rochester Meeting of the American Chemical Society the Council voted "that it is the sense of the meeting that, with President Remsen's consent, the American *Chemical Journal* be incorporated with the *Journal of the American Chemical Society,* provided it can be done under the title of the *Journal of the American Chemical Society,* and without separate pagination."

This proposal has been approved by President Remsen and it has been agreed to add on the title page of our Journal the words "With which is incorporated the American Chemical Journal, founded by Ira Remsen "

At the time of the Rochester Meeting some members of the Organic section expressed a very strong desire that the *American Chemical Journal* should be continued as a separate journal, and made the organ of the Society for the publication of articles in Organic and Biological Chemistry. The *Journal of the American Chemical Society* would, at the same time, become our organ for the publication of articles in General, Physical and Inorganic Chemistry. The title page of the *American Chemical Journal* might read somewhat as follows:

Vol. 51.   American   No. 1,
Chemical Journal
Founded by Ira Remsen

Editor . . . .   Associate Editors . . . .

. . . .
Contents
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Published by the American Chemical Society, Easton, Pa.

The title page of the *Journal of the American Chemical Society* would remain essentially as at present except that the division of organic and biological Chemistry would be omitted.

Shortly after the Rochester Meeting an inquiry was sent out by the Secretary of the Organic Section to the members of the Section. 150 replies have been received. 133 are in favor of separate publication of the *American Chemical Journal;* 17 are opposed.

Several prominent biological chemists have expressed themselves as in favor of separate publication, but no vote has been taken in that section.

I, accordingly, present the following motion for action by the Council:

"That the Board of Directors be requested to arrange for the publication of the *American Chemical Journal* during the year 1914 as the organ of the Society for Organic and Biological Chemistry."

I make the motion to cover a period of only one year because our agreement with President Remsen is such that if reasons should arise which make the continuation of separate publications undesirable we are at liberty to return to the publication of all of the articles in a single journal. If we were to combine the two journals now, it would be so easy to separate them later.

Some of the reasons in favor of separate publication are as follows:

1. Our Journal is already too large for binding in one volume With the addition of the material which now goes to the *American Chemical Journal* the volume will need to be divided and the division proposed will enable any one using the journals to go at once to the right volume for a given article.

2. Some of the best work of American Chemists in the fields of organic and biological chemistry is now published abroad or in other journals of very limited circulation. This is a serious injury to the development of work in these lines and while any change is likely to come gradually, the separate publication of papers of this class would help to that end.

3. For thirty-four years the *American Chemical Journal* has contributed greatly in giving to American chemists an honorable name abroad and in fostering high ideals for chemical research in America. It seems to many of us a great pity that such a journal should cease to exist as a separate journal.

Some of the objections which have been raised against separate publication are:

1. That we cannot afford to send four journals to our members for $10.

Our printers have furnished the following estimate of the cost of separate publication, assuming the material to be published as the same, for an edition of 7500 copies:

Extra binding per issue -	$30
Extra covers per issue	40
Separate mailing	30
	$100

This would be a total expense of $1200 for the year. There need be no extra editorial expenses.

The *American Chemical Journal* now goes to 240 libraries and institutions, and to 103 individuals not members of the American Chemical Society. Assuming that 300 of these should continue as subscribers at $5 a year, it would give us an income of $1500, while the cost of printing and sending these extra 300 copies would be somewhat less than $300. This would care for the extra expense of separate publication. Doubtless something could be secured, also, from advertisements on the covers of the journal.

2. It is objected that some articles belong as much in one journal as in the other. We have classified articles in exactly this way for several years and the question of the

proper place for a given article has very rarely caused any difficulty. It is much more difficult to decide whether an article belongs in the *Journal of the American Chemical Society* or in the *Journal of Industrial and Engineering Chemistry*.

3. It is objected that many of our members do not care for *three* journals even, much less for *four*. If this is really true, there is no objection to allowing any member to stop one of the journals while still paying full dues. There might be some saving to the Society in that way, but I venture to predict it would never be large.

4. When the question of a separate pagination for the divisions of the Journal was brought up a year ago it was objected that we ought not to divide the Journal until there was an opportunity to secure some other journal. We now have such an opportunity and we ought to utilize it in the best way possible

The advantages of separate publication seem to be very considerable and I sincerely hope that it may be given a trial for the coming year.

Respectfully submitted,

(Signed) W. A. Noyes.

Boston, Mass., October 29, 1913.

Dear Dr. Noyes:

I have to acknowledge your letter of the 25th, with copy of your communication addressed to Professor Parsons for submission to the Council, and I must confess to having read the letter with considerable surprise.

While there is possibly, as you say, a difference in form between your present proposal and that which was considered by the Council and by the Directors at Rochester, it seems to be, nevertheless, fundamentally and essentially the same in that it contemplates a division of the journals of the Society and a separate pagination for such matter as is allotted to the *American Chemical Journal* At any rate, I do not see that your present proposal avoids any of the objections which led to the rejection of the plan in the form in which it was brought forward at Rochester

I also feel that your statement, as it stands, requires modification if it is to adequately represent the situation.

Following the recommendation of the Council, it was voted by the Directors, as you say, that with President Remsen's consent the *American Chemical Journal* be incorporated with the *Journal of the American Chemical Society*, provided it can be done under the title of the *Journal of the American Chemical Society* and without separate pagination; and, as you also say, the proposal has been accepted by President Remsen and the Directors and myself regarded the matter as closed.

There were certain very poignant reasons which led to the decision of the Directors, among which was the very strong feeling that having spent so many years in building up the Journal of *the American Chemical Society*, it would now seem suicidal to transfer the bulk of its material to another journal. There was also a strong feeling that in spite of the honorable record of the *American Chemical Journal*, there is at present no real general demand for its continuance. If there were, it would reflect in its subscription list and the present situation would not have arisen

You say that the title page of our own journal would remain essentially as at present, under your plan, but I think that you will admit that the Journal itself would be greatly weakened and its value and standing correspondingly impaired.

I do not think that the postal card ballot conducted by Dr. Hale is entitled to any especial weight in considering the matter, by reason of the extreme inadequacy of the statement submitted to the voters.

I have not at hand the number of members in the Organic Section but I should expect in a vote of this kind that the large majority of replies received would be affirmative, for the members who wanted the thing done would be the ones to vote, and those

who were indifferent would probably not vote at all My recollection is that the Biological Division, as a whole, was distinctly opposed to the separate publication

I note that your proposal is limited to one year but I feel very strongly that we ought not to start any publication unless we can very definitely see our way to its continuance, and having once started there would be many inconveniences in again combining the journals

I think there is no question that we cannot afford to send four journals to our members for $10 The Directors considered this phase of the matter very carefully as also the suggestion that the members be allowed to select three of the four It was felt that this would be a very dangerous proceeding which would not fail to result in great loss to the Society and in increased expense

I regret that I find myself unable to accept your statement of the expense likely to be incurred by the Society if it were committed to the publication of a new separate journal It would certainly not be long before there was a demand for grants to cover editorial expenses, and I believe that the other expenses would very quickly run to a figure far in excess of that named by the printers

However this may be your motion is clearly one which directly involves the finances of the Society and as such falls within the provisions of the vote of the Council at the Baltimore meeting, which you will find on page 32 of proceedings of 1909 Vol 31, reading as follows

"In future no vote involving financial matters shall be taken by mail without being previously submitted to the Board of Directors who shall be allowed three weeks to express an opinion Failure to express an opinion within the stipulated period shall be construed as assent '

Since that vote was passed the relative status of the Directors and Council has undergone great change, and the responsibility for such action as your motion contemplates rests of course with the Directors and must be decided ultimately by them

While, therefore, I feel strongly that the essential subject matter of your motion has already been fully passed upon both by the Council and by the Directors, I am, of course anxious to meet your wishes so far as I can consistently do so As I am, nevertheless, confident that the Directors are not likely to change their position in the matter I hesitate to put the Society to the expense of a Directors' meeting I have, therefore, instructed the Secretary to mail at once to each Director a copy of your motion and the letter in which it is embodied and request them to advise me of their views at once If these replies show any diversity which seems to indicate that a discussion by the Directors might be profitable, I will at once call a Directors' meeting In that case it may very well be that the Board will desire the advice of the Council, but, as you are aware, By-law 3 provides that if the Council be not in session any matter may be decided by the Directors Yours faithfully '

(Signed) A D LITTLE *President*

DIRECTORS' COMMENTS

A D LITTLE—as per preceding letter

M T Bogert "As to separate publication of the *American Chemical Journal* I believe it is to the best interests of the Society not to do so, and that, therefore, there is no occasion for reconsidering the action of the Directors and of the Council "

A P Hallock "I do not see any reason for changing my opinion, nor any good reason why it should be again submitted to the Council '

Alexander Smith "I think that President Little's letter states the matter with absolute correctness, and I can only say ditto to what he says Possibly to avoid future friction, it would do no harm to send the matter to the Council, together with the Directors' present opinion "

T. J. Parker: "Referring to letter of Prof. W. A. Noyes regarding the separate publication of the *American Chemical Journal*, in view of the action of the Council and Directors at the Rochester meeting, I do not see how I can change my vote on the question."

E. G. Love: "In my opionion there is nothing in the communication from Prof. Noyes which calls for a reference of the matter in question to the Council after the action taken by that body at the Rochester meeting. If, however, the motion of Prof. Noyes should be submitted to the Council and should be acted upon favorably, I have serious doubts whether the affair could be successfully financed by the Society."

W. D. Bigelow: "I have read Dr. Little's report and Dr. Noyes' letter and fully agree with President Little's reply.

"In view of the obligations of the Society with respect to its present journals, which we must meet, I think a grave mistake would be made should we carry out the wishes of Dr. Noyes.

"After carefully considering the matter, I feel that Dr. Noyes has greatly under-estimated the immediate cost of publishing the two Journals separately, and in addition we must not forget that, if undertaken, additional editors will be necessary in the near future."

William Brady: "I feel sure it is the desire of all of the Directors at all times to act in accordance with the wishes of the Council. The Council as convened in Rochester did act. The question might be raised that there were only 49 members of the Council present and possibly all of the Council, consisting of something over 100 members, would act differently. This being the case, and a desire on my part to learn the feeling of the entire Council in the matter, I would favor a letter ballot."

Charles L. Parsons. "The expense curve of the Society is mounting much faster than the membership.

"To increase the dues would, in my opinion, decrease the income.

"A fourth journal can be published only at the expense of the other three One must consider the future, not simply the present. The articles in the present *American Chemical Journal*, together with the organic and biological matter in our own journal, would make a journal fully equal in size to the present Journal *of the American Chemical Society*. If the *American Chemical Journal* alone grew, 'our journal' would alone be unworthy of us. If the depleted *Journal of the American Chemical Society* grew again to its present size through the efforts of the general, physical, and inorganic chemists, the increased cost, instead of the $1200 mentioned would be approximately, $11,400, the 1913 cost of the *Journal of the American Chemical Society*, for no claim has been made that the editorial work could be carried without extra expense for more than a single year.

"The funds asked for by the three editors for 1914 are more than $9000 over the last budget for our present three journals. There is no income in sight to meet even this increase and a fourth journal (a fifth or sixth might be desired with equal unanimity by other groups of specialists) is, in my opinion, out of the question.

"Of the 343 subscribers referred to by Dr. Noyes, only 67 are not receiving the *Journal of the American Chemical Society*. Of these 21 are booksellers, whose clients are unknown. Only one is a library or educational institution in Germany, and two in France."

On November 28th, at Dr. Noyes' request, a second letter from him giving additional arguments in favor of continuing the *American Chemical Journal* was enclosed in the regular communications to the Council for election of officers of that date.

The ballot on this communication was counted on December 12th, by a

committee consisting of W. F. Hillebrand, S. S. Voorhees, and C. L. Parsons, with the following results:

In favor of W A Noyes' motion	16
Opposed	65
Blank	1
Illegal .	3
	—
Total	85

C L PARSONS, *Secretary.*

MEMBERS ELECTED BETWEEN NOVEMBER 15 AND DECEMBER 15.

Adiassewich, Alexandre, Nadejdiuskaia, Russia.
Alves, Henry L., 855 Hampshire St., San Francisco, Calif.
Armstrong, Bruce, Box 42, Dixon, Ill
Auger, Charles L., Paterson, N. J.
Back, Robert, Bureau of Mines, Washington, D. C,
Bacon, Rudolph F., 805 Crescent Place, Chicago, Ill
Bailey, J. R., University Station, Austin, Texas.
Banigan, Frank, 406½ Elm Street, Reno, Nevada.
Becker, Reinhold S., Kodak Park, Rochester, N. Y.
Bick, George N., 348 60th Street, Brooklyn, New York.
Blucher, Joseph C., Box 58, New York University, University Heights,
N. Y. City.
Booth, L. M., 58 Hudson Street, Jersey City, N. J.
Briggs, John, 45 Purchace St., Boston, Mass
Bullock, Jesse L., 12 Merrill Street, Cambridge, Mass.
Burt, Raymond Arthur, 82 Morgan St , New Bedford, Mass
Carter, Frederick E., Fuel Testing Plant, Division St., Ottawa, Ont., Can.
Caugherty, W. E., Allegheny Steel Co., Brackenridge, Pa.
Cullen, Glenn E., Rockefeller Institute, 66th St. and Ave. A, New York
City.
Dakin, H. D., 819 Madison Avenue, New York City.
DuPont, Coleman, Wilmington, Delaware.
Eastman, Harold M., Durham, New Hampshire.
Eaton, Edward N., 5620 Drexel Avenue, Chicago, Illinois.
Ellett, W. B., Agricultural Experiment Sta., Blacksburg, Va.
Enright, Bernard, 233 North 4th St., Allentown, Pa.
Erdoes, Julius, 1100 Brook Avenue, New York City.
Fry, William H., Bureau of Soils, Washington, D. C.
Funchess, M. J., Auburn, Alabama.
Funkhouser, S. P., P. O. Box 311, Ithaca, N. Y.
Geyler, F. O., Mentz Apartments, Niagara Falls, New York.
Gillespie, Louis John, 1424 R. Street, N. W., Washington, D. C.
Green, Alva I., Univ. of South Carolina, Columbia, South Carolina.
Guiterman, Kenneth S., 465 West End Avenue, New York City.
Henderson, Lawrence M., 5437 Ellis Avenue, Chicago, Ill.
Herz, Nathaniel, Box 847, Lead, South Dakota.
Hirschfelder, Arthur D., University of Minnesota, Minneapolis, Minn.
Holden, H. Chester, Durham, New Hampshire.
Hobby, Amos K., 51 Mt. Auburn St., Cambridge, Mass.
Huddle, W. P., 904 Hume Mansur Building, Indianapolis, Indiana.
Hughes, John L., Connecticut Agricultural College, Storrs, Conn.

Hursh, Ralph K., 905 South 6th Street, Champaign, Illinois.
Huthsteiner, Hans, 120 Park Avenue, Schenectady, New York.
Hynes, J. A., 158 West Harrison Street, Chicago, Illinois.
Johnston, Angus J., 4237 Broadway, Chicago, Illinois.
Jones, G. Lloyd, P. O. Box 761, Middletown, Conn.
Knight, Charles Clark, Lewiston Bleaching and Dye Works, Lewistown, Me.
Knudson, Arthur, 437 West 59th Street, New York City.
Koelliker, Herman Michael, 2022 East 105th Street, Suite 11, Cleveland, Ohio.
Lake, W. W., 1369 Fry Avenue, Cleveland, Ohio.
Lower, John Royal, 89 Chittenden Avenue, Columbus, Ohio.
Lundahl, S. F., 421 South Trumbull Avenue, cor. Congress St., Chicago, Ill.
McWilliams, Charles K., Box 482, Pullman, Washington.
Meyers, Herman B., 15 South Market St., Chicago, Ill.
Miller, C. F., Bureau of Soils, Washington, D. C.
Miller, Harry M., Apartment 43, 1440 W Street, N. W., Washington, D. C.
Mitchell, Harry G., Hanover, New Hampshire.
Mowry, Leland B., Copperhill, Tenn.
Munn, William K., 6428 Dante Avenue, Chicago, Ill.
Ottobre, V. Emanuel, 216 122nd Street, New York City.
Palmer, Ralph M., 4014 Forest Boulevard, East St. Louis, Ill.
Patterson, Lamar G., Box 174, Montgomery, Alabama.
Ping, America V. (Miss), Olvidar Building, Arecibo, Porto Rico.
Plaut, Edward, 28 East 76th Street, New York City.
Porter, W. E., 427 Gas and Electric Building, Denver, Colorado.
Priestley, J. G., 515 Broadway, N., Seattle, Washington.
Propach, C. H., 2340 Commonwealth Avenue, Chicago, Ill.
Reeve, James H., Box 235, Americus, Georgia.
Richards, Wayne V., Union City, Michigan.
Richter, Herman William, 1 Warwick Park, Cambridge, Mass.
Ringer, Adolph Irving, New Medical Lab., Univ. of Penn., Philadelphia, Pa.
Satler, Louis L., Jr., Glenshaw, Pennsylvania.
Saxton, Blair, 37 Lake Place, New Haven, Connecticut.
Schmidt, H. B., The Joslin-Schmidt Co., Sta. P, St. Bernard, Ohio.
Seeman, F. J., U. S. P. O. Box 771, Shanghai, China.
Shellabear, Hugh Percy, 703 California Ave., Pullman, Washington.
Shepard, M. G., 316 Huntington Avenue, Boston, Mass.
Sillman, Maxwell, 857 North 6th St., Philadelphia, Pa.
Smith, F. Clayton, 319 West 9th St., Elyria, Ohio.
Smith, Erwin J., Menando, Albany, New York.
Smith, Joseph G., Bureau of Soils, Washington, D. C.
Sprague, P. E., 84 West 9th Avenue, Columbus, Ohio.
Stein, Leo, 410 West 13th Street, New York City.
Stevenson, Albert Fletcher, The Woodward Apartments, Washington, D. C.
Sweet, Harold A., 414 Court Street, Syracuse, N. Y.
Taber, George H., Frick Building Annex, Pittsburgh, Pa.
Taylor, Fred A., 126 North Avenue, New Rochelle, N. Y.

Taylor, George G., Summerlea Apartments, Summerlea and Elmwood Sts., Pittsburgh, Pa.

Todd, James, Sewickley, Allegheny County, Pa.

Townsend, Jackson, Lake Butler, Florida.

Upton, Howard S., care Atlantic Insulated Wire and Cable Co., Stamford, Connecticut.

Vitoria, Eduardo, Director del Laboratorio Quimico del Ebro, Tortosa, Tarragona, Spain.

Weidmann, Walter L., 842 Monmouth Street, Gloucester, N. J.

Wheaton, Theodore, Jr., 518 N. High Street, Millville, N. J.

White, Wilbur S., Room 418, City Hall, Cleveland, Ohio.

Whitham, Gilbert Shaw, Ofe Cilia, Carmen Alto, Antofugasta, Chili.

Zoller, Harper F., University of Puget Sound, Tacoma, Washington.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

UNIVERSITY OF MISSOURI SECTION.

The 40th meeting of the University Section was a short business meeting held on August 22, at 5 P.M.

The 41st meeting of the Section was held Sept. 30. Prof. R. B. Moore, of the United States Bureau of Mines, spoke on the work of the Bureau of Mines.

The 42nd meeting was held November 15. Dr. L. E. Wise spoke on Chinese Wood Oil.

The 43d regular meeting of the Section was held on Nov. 28th. Dr. A. Gulick spoke on "Some Points Concerning the Results of Over-nutrition." O C SMITH, *Secretary.*

NEBRASKA SECTION.

The 70th regular meeting of the Section was held on Oct. 24, 1913, at the University of Nebraska at Lincoln.

Dr. F. W. Upson, who is now in charge of the Nebraska Experiment Station, gave an illustrated lecture on the "Electrolytic Theory of Oxidation and Reduction." C J. FRANKFORTER, *Secretary.*

KANSAS CITY SECTION.

The 95th regular meeting of the Section was held at Kansas City, Mo., October 25, 1913. The program of the evening consisted of an address by Dr. W. S. Wheeler, Health Commissioner of Kansas City, on "Tuberculosis," and an illustrated lecture by Prof. W. A. Whitaker, of the University of Kansas, on "Chilean Nitrates and Trinidad Asphalt."

The 96th regular meeting of the Section was held at Lawrence, Kans., November 22, 1913. The following papers were read:

"Medical Frauds as Exposed by Chemical and Pharmaceutical Methods." Prof. L. E. Sayre.

"Some Rules and Specifications Governing Transactions in Soapmaking Materials," W. J. Reese.

The annual banquet and election of officers was held Dec. 6, 1913. Dr. W. A. Noyes, of the University of Illinois, gave an address on the topic, "The Electron Theory."

Officers for 1914 were elected as follows: President, L. D. Havenhill; Vice-President, Roy Cross; Councilor, E. H. S. Bailey; Secretary-Treasurer, W. B. Smith, 24 Federal Building, Kansas City, Kansas; Assistant Secretary, W. A. Whitaker. W B SMITH, *Secretary.*

ST. LOUIS SECTION.

The Section met November 10, 1913, at the Missouri Athletic Club.

Mr. Marshall W. Cox read a paper on "Lithium Perchlorate at High Temperatures," in which he described some of the atomic-weight determinations of Prof. T. W. Richards.

President Monfort called the December meeting to order on December 8, 1913.

Mr. C. F. Carrier, Jr, addressed the Section on, "Metallic Sodium, Its History, Manufacture and Uses."

The following officers were elected: President, Dr. Leroy McMaster; Vice-President, A. C. Boylston, Treasurer, E. J. Ericson; Secretary, George Lang, Jr.; Councilor, W. F. Monfort. GEO LANG, JR, *Secretary*

IOWA SECTION.

The meeting of the Section was held in the Chemistry Building, Iowa State University, November 15th.

The following papers were presented: Dr. Nicholas Knight, "A Problem in Soil Chemistry at Sylvan Beach, New York." Dr. J. N. Pearce, "Conductivity in Organic Solvents." Dr. W. J. Karslake, "The Paraxylenenitrosulphonic Acids." Dr. R. R. Renshaw, "The Detection of Small Amounts of Neurine in Chlorine." Dr. R. R. Renshaw, "Hydrolytic Dissociation of Nitrobenzene."

Miscellaneous reports. J A WILKINSON, *Temporary Secretary.*

ROCHESTER SECTION.

Meetings were held at the University of Rochester on November 17 and December 1, 1913. On November 17, Mr. Eberlin, of the Eastman Kodak Co., spoke on "The Use of the Hydrogen Electrode in the Determination of the Acidity of Weak Acids," and Mr. Adkins, of the Vacuum Oil Co., spoke on "The Determination of the Flash Point of Oils." On December 1, Dr. Chambers, of the University of Rochester, discussed the "Grignard Reaction," and Mr. Little, also of the University, discussed

the "Use of Finely Divided Nickel in the Hydrogenation of Organic Compounds."

The December meeting was held Monday, December 15, 1913, at the University of Rochester. Dr. L. E. Sheppard spoke on "The Scope of Colloidal Chemistry."

Wm H Earle, *Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

The November meeting was held November 18th. The officers were elected for the ensuing year as follows: Chairman, S. W. Parr; Vice-Chairman, Geo. McP. Smith; Councilors, Edward Bartow, E. W. Washburn; Secretary, D. F. McFarland; Treasurer, D. A. MacInnes.

The address of the evening was given by Professor W. D. Harkins, of the Department of Chemistry in the University of Chicago, on the subject "The Intermediate Ion Hypothesis and the Chemistry of Salts of Higher Types."

D F McFarland, *Secretary*

CINCINNATI SECTION.

The 188th regular meeting was held at the Ohio Mechanics' Institute Nov. 19.

The Committee reported on "Spring Meeting."

Mr. F. L. Baringer, of the Eagle White Lead Company, gave a talk on "The Technology of Lead Pigments."

The 189th regular meeting was held at the University of Cincinnati, December 17th.

Mr. H. E. Howe, of the Bausch & Lomb Optical Co., gave an illustrated lecture on "Notes on the Manufacture of Some Scientific Instruments," in which special stress was laid on glass. Mr. Howe brought with him many interesting samples.

The usual informal dinner preceded the meetings.

Stephan J Hauser, *Secretary*

CLEVELAND SECTION.

The regular monthly meeting of the Section was held in Adelbert College, November 19th.

Mr. William H. Alexander, the local forecaster of the weather, gave an illustrated address at this meeting on the subject, "The United States Weather Bureau and Its Work."

W R Eiffer, *Secretary*.

PITTSBURGH SECTION.

The 102nd regular meeting of the Section was held at the University of Pittsburgh, November 20th.

Program: 1. "The Refining of Petroleum," Harry H. Willock, General Manager Waverly Oil Works, Pittsburgh, Pa. 2. "The Use of Scientific Testing Instruments in the Industries," Frank R. Kelley, Pittsburgh Representative of the Taylor Instrument Co.

The Director of the Mellon Institute of Industrial Research, University of Pittsburgh, invited the members of the American Chemical Society to attend a special meeting of the Section at which an address was given by Dr. W.·R. Whitney, Director of the Research Laboratories of the General Electric Company, on "Some Recent Investigations Carried· Out in the Laboratories of the General Electric Company."

The 103rd regular meeting of the Pittsburgh Section was held at the University of Pittsburgh, December 18th.

Program: 1. "Present-Day Metallurgical Problems," D. A. Lyon, Metallurgist, U. S. Bureau of Mines." 2. The Brass Foundry of the Future; with Notes on the Use of Pyrometers in Brass Founding," C. P. Karr, Metallurgist, U. S. Bureau of Standards.   Irving C. Allen, Secretary

INDIANA SECTION.

The Indiana Section of the Chemical Society met in the Science Building of Eli Lilly & Co.'s plant, Nov. 21. Mr. Frederick C. Atkinson gave á talk on the universal language "Esperanto." Dr. W. M. Blanchard, of DePauw University, gave an illustrated lecture on his trip abroad and on chemistry in the German· universities.   A. B. Davis, Secretary.

COLUMBUS SECTION.

Mr. L. D. Vorce, President of the Society of Detroit Chemists and Manager of the Wyandotte Plant of the Pennsylvania Salt Works, addressed the Section November 21, on "Progress of Electro Chemistry in the United States."   D. J. Demorest, Secretary.

LOUISIANA SECTION.

The seventy-first meeting was held at the Louisiana State Museum, November 21, 1913. The following program was given:
"Theories of Valence," H. W. Moseley, M.Sc. "The Absorptive Power of Asbestos for Organic Coloring Matters," R. G. Meyers, M.Sc.
J Heath Lewis, Secretary.

SOUTHERN CALIFORNIA SECTION.

This Section met on Friday evening, November 21, 1913. The usual informal dinner preceded the meeting. The following papers were presented:
"Plant Food and Irrigation Water in California," Mr Alfred Smith, Pomona College. "The Effect of Freezing on the Chemical Composition of Oranges," Mr. H. D. Young, Whittier Pathological Laboratory.
Walter L. Jordan, Secretary.

MINNESOTA SECTION.

The 45th regular meeting of the Section was held in the University of Minnesota on November 21, 1913. Dean G. B. Frankforter gave a paper on. "Some New Phases of Catalysis." Mr Earl Pettijohn was elected Treasurer, vice C. F. Sidener, resigned. Attendance 30.
W. H. Hunter, Secretary.

SYRACUSE SECTION.

On Friday, November 21, a meeting of the Section was held at the Syracuse College of Medicine Building.

Dr. A. W. Browne, Professor of Inorganic and Analytical Chemistry, Cornell University, addressed the Section on "Some New Facts Concerning Ammonia and the Higher Hydronitrogens."

At the December 12th meeting, Mr. H. E. Howe, Chief Chemist of the Bausch and Lomb Company, and councilor from the Rochester Section, spoke on "Glass and Notes on the Manufacture of Optical Instruments."

H B KIPPER *Secretary*

WISCONSIN SECTION.

The December meeting of the Section was held in the Chemistry Building, December 10, 1913. Professor O. P. Watts spoke on "Electroplating."

The Following officers were elected: Chairman, H. C. Bradley; Vice-Chairman, J. H. Mathews; Councilor, J H Walton, Jr., Secretary, A. E. Koenig; Treasurer, W. E. Tottingham.

P W CARLETON *Secretary*

SECTION OF WESTERN NEW YORK.

The November meeting was held at the Niagara Club, on November 24th. Mr. Maximilian Toch lectured on "Chemical Engineering, New and Old, Illustrated."

The December meeting was held on Dec. 17th, at the University of Buffalo.

Papers were read by Mr. Henry Bowen on "Some Features of the Acid Industry in America," and by Mr. E. M. Sergeant on "The Potash Business."

The members met for an informal dinner before the meeting.

WALTER WALLACE *Secretary*

WASHINGTON SECTION.

The 231st meeting was held at the Cosmos Club, November 25th. A meeting of the Executive Committee was held in the council room.

Dr. P. A. Levene, of the Rockefeller Institute for Medical Research, New York City, lectured on "The Chemistry of the Nucleic Acids."

The 232nd meeting was held at the Cosmos Club, December 11th. A meeting of the Executive Committee was held in the council room. A program followed:

J. G. Fairchild, of the Bureau of Mines, "Electro-analysis of the Copper Alloys," and "The Iodometric Determination of Iron." W. D. Collins, of the Bureau of Chemistry, "Radioactivity of Virginia Mineral Waters." G. A. Menge, of the Hygienic Laboratory, "The Preparation of Amino-nitriles." G. B. Spencer, of the Bureau of Chemistry, "Goettingen."

ROBERT B. SOSMAN, *Secretary*.

DETROIT SECTION.

The regular meeting of the Detroit chemists occurred on Friday, Nov. 28th, in the Stevens Building.

Prof. Alfred H. White, of the Chemical Engineering Department of University of Michigan, spoke upon "Under what Circumstances can Portland Cement be Considered a Reliable Building Material for Permanent Structures?" (Lantern slides.)   ROBERT T HARRIS *Secretary*

OREGON SECTION.

The regular November meeting and annual election was held at the Hazlewood Café, 310 Washington St., Portland, Saturday evening, November 29.

C. E. Travillion presented a paper on "Fertilizers," and V. P. Edwards spoke on "Chemical Control of a Lead Smelter," during the evening. The meeting was preceded by a dinner.   F. A OLMSTED, *Secretary*

UNIVERSITY OF MICHIGAN SECTION.

The second Fall meeting was held Tuesday afternoon, December 2nd, in the Chemistry Building. Dr. J. E. Harris addressed the Section on "Selective Asborption by Soils."   W G SMEATON, *Secretary*

LEXINGTON SECTION.

The Section held its 12th regular meeting in the Kentucky Agricultural Experiment Station, Friday afternoon, December 5, 1913.

Program for the meeting was as follows. Report of Annual Convention of the Association of Official Agricultural Chemists, by S. D. Averitt and B. D. Wilson.

The following officers were elected: Chairman, Dr. F. E. Tuttle, State University, Lexington, Ky.; First Vice-Chairman, Dr. R. N. Maxon, State University, Lexington, Ky.; Second Vice-Chairman, Mr. S. D. Averitt, Ky. Agricultural Experiment Station, Lexington, Ky.; Councilor, Prof. F. E. Clark, Central University, Danville, Ky.; Secretary and Treasurer, Dr. G. D. Buckner, Ky. Agricultural Experiment Station, Lexington, Ky.   LINWOOD A BROWN, *Secretary.*

CONNECTICUT VALLEY SECTION.

The 20th regular meeting of the Section was held at Springfield, Saturday afternoon and evening, December 6th. The afternoon was spent in visiting the new laboratory of the Emerson Laboratory Co., the laboratory and plant of the Baker Extract Company, and the plant of the Springfield Gas Co.

Following a dinner, the regular program followed, *viz.:* 1. "New Sources of Paper-making Fibre and the Determination of Their Commercial Value," H. P. Carruth. 2. "Organization and Work of the Chemical

Department of the Massachusetts Experiment Station," Philip H. Smith.
3. "The Water Content of Vanilla Beans." B. H. Smith.

<div align="right">F P GILLIGAN, <i>Secretary.</i></div>

CHICAGO SECTION.

The December meeting of the Chicago Section was held December 12th. The subject of the evening was "Color Photography," by Prof. J. H. Mathews, Professor of Physical Chemistry, University of Wisconsin, Madison, Wis. The members of the Section held the usual informal dinner before the meeting.

<div align="right">D K FRENCH <i>Secretary</i></div>

NEW YORK SECTION.

The third regular meeting of the session 1913–14 was held in conjunction with the New York Sections of the Society of Chemical Industry, the American Electrochemical Society, and by special invitation, the American Institute of Chemical Engineers, in Rumford Hall, on Dec. 12th.

After the election of local councilors, papers on the "Welfare and Safety Work in American Chemical Industry," were presented by Miss Florence Hughes, member of General Staff, Sociological Work, New Jersey Zinc Company, Howard Lyon, Experimental Department, Welsbach Company, Charles P Tolman, Chairman Manufacturing Committee, National Lead Company, and Francis D. Patterson, Director of the Department of Sanitation and Accident Prevention, Harrison Bros. & Co., Inc.

<div align="right">C M JOYCE <i>Secretary</i></div>

NEW HAVEN SECTION.

There was a meeting of the Section at the Graduates' Club on December 12, 1913. The usual dinner was served at 6.45 P.M.

Professor L. W. Bahney addressed the Section on the "Extraction of Gold from Low Grade Ores."

<div align="right">GEORGE S JAMIESON <i>Secretary</i></div>

CALIFORNIA SECTION.

The seventy-fourth regular meeting of the California Section was held at the University of California Club, December 13th.

The paper of the evening was on the "Workings of the California Insecticide Law," by George P. Gray.

The meeting was preceded by a dinner.

<div align="right">BRYANT S DRAKE, <i>Secretary</i></div>

NASHVILLE SECTION.

The 21st meeting of the Section was held in Furman Hall of Vanderbilt University on Friday evening, December 19th, at 8 o'clock. The program included the following papers or addresses:

"The Planetesimal Hypothesis of the Origin of the Earth," Dr. A. H. Purdue, State Geologist.

<div align="right">EUGENE G GRAS, <i>Secretary</i></div>

The December meeting was held in the Physics Lecture Room, State Normal College, on December 19th. The following lecture was presented: "The Rare Earths," by Professor L. M. Dennis, of Cornell University.

C F HALE *Secretary*

DECEASED.

Arthur Edgar, White Haven, Pa., on Nov. 15, 1913.

Louis D. Gilbert, of Santa Rosa, California, in St. Louis, June 15, 1913.

H. F. Walker, Lewistown, Pa., May 9, 1913.

ANNUAL TABLE OF CONSTANTS.

Volume III of the Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological, published by the International Commission of the VII and VIII International Congress of Applied Chemistry is now in press and will be issued in the first half of 1914. A descriptive circular with references to reviews of previous volumes may be secured on application to The University of Chicago Press.

The subscription to Volume III is now opened and *will be closed March 31, 1914*. The names of subscribers should be sent to The University of Chicago Press, the American Agent for the distribution of the Annual Tables. Subscriptions are payable to The University of Chicago Press at the time of publication.

The subscription price of Volume III will be the same as for Volume II, namely, $6 for the unbound copy, $6.80 for the bound copy (carriage free). Members of contributing societies (*The American Chemical Society, The American Electrochemical Society, The Society of Chemical Industry, The American Academy of Arts and Science, The National Academy of Science*) and of contributing manufacturing establishments, are entitled to a discount of 20% (but not on the binding) and will receive the volume unbound for $4.80, bound for $5.60 (carriage free), *provided their subscriptions are received* by March 31, 1914. After March 31, 1914, the price will be raised to $6.40 (unbound) and $7.20 (bound), a charge will be made for carriage and no discounts will be allowed.

JULIUS STIEGLITZ, The University of Chicago.
EDWARD C. FRANKLIN, Leland Stanford University.
HENRY G. GALE, The University of Chicago.
ALBERT P. MATHEWS, The University of Chicago.
Commissioners for the United States.

Proceedings.

COUNCIL.

President Little appointed the following Committee on Endowment but acceptances were received too late for the January JOURNAL:

George D. Rosengarten, Chairman; Isaac K. Phelps; George F. Kuntz.

MEMBERS ELECTED BETWEEN DECEMBER 15 AND JANUARY 15.

Acker, Frank J., 12 West Kinzie St., Chicago, Illinois.
Agazim, T., 1428 N. Maplewood Ave., Chicago, Illinois.
Akers, A., 1206 Williamson Bldg., Cleveland, Ohio.
Alexander, H. H., Maurer, New Jersey.
Ambler, Joseph A., Wolfville, Nova Scotia.
Anderson, Leon E., 34 Tecumseh St., Dayton, Ohio.
Andrews, J. Clarence, Iowa City, Iowa.
Axelrad, Sol, 358 East 57th St., New York City.
Bacon, Charles B., Bureau of Chemistry, Washington, D. C.
Baldeschwieler, Emile L., 201 West 24th St., New York City.
Balz, E. H., 964 South High St., Columbus, Ohio.
Barmeier, Floyd E., 1403 Syndicate Trust Bldg., St. Louis, Missouri.
Barrows, Lewis O., Beta Theta Pi, Orono, Maine.
Bartling, F. W., Central Carmen, Vega Alta, Porto Rico.
Bastone, Harry J., 1316 South Roekland St., Calumet, Michigan.
Becker, A. J., 217 Green Ave., Champaign, Illinois.
Bennett, Harold S., 1 Grove Place, Ithaca, New York.
Bernard, Pierre Arnold, 145 Christie St., Leonia, N. J.
Beutner, R., 106 East End Ave., New York City.
Bichowsky, F. Russell V., 2329 Bancroft Way, Berkeley, California.
Blackmarr, Frank H., 25 Washington St., Chicago, Illinois.
Bohlmann, E. F., 693 Layton Blvd., Milwaukee, Wisc.
Bole, G. A., Box 593, Alfred, New York.
Bonney, Robert D., 535 Newberry St., Boston, Mass.
Braley, S, A., 916 West California Ave., Urbana, Illinois.
Braude, Harry, Pennsylvania Glue Co., Springdale, Allegheny Co., Pa
Brown, Alan L., The Knol', Ithaca, New York.
Buist, George Alexander, 1026 Pendleton St., Greenville, South Carolina.
Callenbach, J. A., 131 Maple Terrace, Merchantville, New Jersey.
Cann, Jessie Yereance, 112 Brunswick St., Newark, New Jersey.
Carman, J. S., 903 Grattan St., Los Angeles, California.
Carnahan, Glen, 3430 Michigan Ave., Chicago, Illinois.
Carpenter, Laurence E., 110 Grand St., Newburgh, New York.
Carter, Carnie Blake, Chapel Hill, North Carolina.
Carter, W. A., 5 Johnson St., Lynn, Mass.
Cash, Gentry, Whiting, Indiana.
Chapin, Arthur B., 843 Lill Ave., Chicago, Illinois.
Charlton, E. E., 916 West California Ave., Urbana, Illinois.
Cheruoff, Lewis Hill, 555 Elm St., New Haven, Connecticut.
Clark, Arthur H., 70 Linden Ave., Malden, Mass.
Clark, Hugh, 625 Clyde St., Pittsburgh, Pennsylvania.
Coffman, Elwood Foster, 1163 Princess Ave., Camden, New Jersey.

Coopersmith, S., care of Collegiate Club, 1501 11th St., N. W., Washington, D. C.

Cotton, W. J., 523 Bryant Ave., Chicago, Illinois.

Davidson, Wilmot A., 54 Alexander St., Toronto, Ontario, Canada.

Dawson, Henry Royal, Beechlands, Park Ave., Ashton-on-Mersey, Cheshire, England.

Dean, Ernest Woodward, 692 Yale Station, New Haven, Connecticut.

DeCelle, O. A., 5310 Indiana Ave., Chicago, Illinois.

DeCew, Judson A., 903 McGill Bldg., Montreal, Canada.

Detwiler, J. G., Box 210, Port Arthur, Texas.

Dodd, Sidney R., 45 St. Botolph St., Boston, Mass.

Dore, Edward A., Box 766, Orono, Maine.

Dunbar, Orville Derward, Box 260, Huron, South Dakota.

Evans, Jr., S. S., Williamstown, Mass.

Falk, Nils B., Box 24, Station A, Elizabeth, New Jersey.

Faragher, Paul V., 1329 Vermont St., Lawrence, Kansas.

Feagley, C. C., Harrison Brothers and Co., Philadelphia, Pa.

Finkelstein, Leo, 830 Lowell Place, Chicago, Illinois.

Fiske, Cyrus Hartwell, 291 Brookline Ave., Boston, Mass.

Ford, J. B., 207 East University Ave., Waxahachie, Texas.

Forst, Leo B., 411 Government Bldg., Cincinnati, Ohio.

Franck, Paul, 317 West 119th St., New York City.

Franken, Frans, 412 North Second St., Mankato, Minnesota.

Furlong, Irving, Arrow Rock, Idaho.

Gallun, Arthur H., 1000 North Water St., Milwaukee, Wisconsin.

Gazzolo, Frank H., 1357 Astor St., Chicago, Illinois.

Giddings, Donald S., 5658 Blackstone Ave., Chicago, Illinois.

Glattfeld, John W. E., 5731 Kenwood Ave., Chicago, Illinois.

Goetschius, Roland B., Box 136, Corbett, Delaware County, New York.

Goodpasture, J. M., 32 Rodney Dormitory, Univ. of Penn., Philadelphia, Pa.

Gram, Carl W., Walter Baker & Co., Ltd., Milton, Mass.

Greathouse, Ruth C., Box 11, Sta. A., R. F. D. 4, Washington, D. C.

Gregg, Wells K., 1115 Mellon St., Pittsburgh, Pa.

Hall, Arthur E., 5113 Capitol Ave., Omaha, Nebraska.

Hamilton, W. C., 8 Parkland Place, St. Louis, Missouri.

Hartupee, Carl A., Roofing Department, Diem and Wing Paper Co., Cincinnati, Ohio.

Hartzell, F. Z., Geneva Experiment Station, Geneva, New York.

Hauss, David J., Aurora, Indiana.

Hauth, Louis H., 935 East College St., Iowa City, Iowa.

Hecht, Selig, Bureau of Chemistry, Washington, D. C.

Hedges, Charles Cleveland, care of Texas Agricultural and Mechanical College, College Station, Texas.

Heritage, Clark C., 5709 Midway Park, Chicago, Illinois.

Hess, Frank Galen, 7723 Mulford St., Pittsburgh, Pa.

Heyward, Jr., J. B., 4024 Lyon Ave., Oakland, California.

Hines, Edward G., 53 West 8th Ave., Columbus, Ohio.

Hirsh, Louis, 1507 West Elburn Ave., Chicago, Illinois.

Hitchcock, Robert B., 720 Carolina St., Gary, Indiana.

Hobbs, William Henry, Box 483, Danville, Illinois.

Hogaboom, George B., 82 Lake St., New Britain, Connecticut.

Holtz, Henry F., Pullman, Washington.
Hood, Homer T., 417 East Liberty St., Ann Arbor, Michigan.
Hook, Frank W., 3743 Indiana Ave., Chicago, Illinois.
Howell, Spencer P., 202 Gray Apartments, Wilkinsburg, Pennsylvania.
Hubbell, John P., Garden City, New York.
Huffman, Carl H., Box 138, Meadowbrook, West Virginia.
Hulett, Edwin L., Canton, St. Lawrence County, New York.
Hung Yee, Tang, 609 East Jefferson St., Ann Arbor, Michigan.
Isaacs, Aaron, Bureau of Standards, Washington, D. C.
Jacobs, Benjamin R., Bur. of Chemistry, Washington, D. C.
Jones, Lucius H., 1148 Western Ave., Los Angeles, California.
Jones, Norden R., Gas Works, Foot of Seneca St., Utica, New York.
Judd, Harold D., 7 Onondaga Place, Syracuse, New York.
Keane, L. A., 311 Farm St., Ithaca, New York.
Kemler, W. H., P. O. Box 214, Johnson City, Tennessee.
Kerr, William M., 712 LaFayette Bldg., Philadelphia, Pa.
Kiphinger, Claude C., 416 Douglas Ave., Ames, Iowa.
Knoedler, E. L., 110 Brown St., Gloucester City, New Jersey.
Kohler, Elmer P., 12 Prescott Hall, Cambridge, Mass.
Krawczak, John C., 801 7th Ave., Milwaukee, Wisconsin.
Krieble, Vernon K., Department of Chemistry, McGill Univ., Montreal,
Canada.
Kyriakides, L. P., 7 Bigelow St., Cambridge, Mass.
Laird, William R., 126 Westbourne Lane, Ithaca, New York.
Lamar, Philip R., Southern Cotton Oil Co., Savannah, Ga.
Lambie, J. M., 41 East Bean St., Washington, Pa.
Landgren, J. F., 226 Beresford Ave., Highland Park, Michigan.
Leitch, Harold W., North Andover, Massachusetts.
Lieb, Lloyd L., 2872 Folsom St., San Francisco, California.
Long, Walter S., 942 Mississippi St., Lawrence, Kansas.
Loo, Ming Ying, 452 Vine St., South Bethlehem, Pa.
Lutts, Carlton G., 99 North Common St., Lynn, Mass.
Lyder, Ernest E., 1500 New Hampshire St., Lawrence, Kansas.
MacDonnell, Charles, 269 8th St., Jersey City, N. J.
MacLean, A. Reginald M., Chem. Bldg., McGill University, Montreal,
Canada.
Magnus, Carl, Sigma Nu House, Orono, Maine.
McClester, T. F., Box 232, Bound Brook, New Jersey.
McCool, William F., 788 McDonough St., Brooklyn, New York.
McCrosky, C. R., 17 West Fountain Ave., Delaware, Ohio.
McMahon, George F., 104 Ann St., Hartford, Conn.
Mickel, Clarence W., 25 North Converse Hall, Burlington, Vermont.
Morgan, John C., 108 Cook St., Ithaca, New York.
Muhleman, George W., The Methodist University, Guthrie, Oklahoma.
Myers, Rollin G., Sta. 20, care of Tulane University, New Orleans,
Louisiana.
Nagle, Jr., Harry C., 3018 North Broad St., Philadelphia, Pa.
Nasmith, Mungo E., 111 Heath St., Toronto, Canada.
Nees, A. R., 129 York St., Brooklyn, New York.
Nutting, Willard H., 2600 Bancroft Way, Berkeley, California.
Oak, Malcolm H., Beta Theta Pi, Orono, Maine.
Odlum, W. Julian, Ardmore, Bray, County Wicklow, Ireland.

Ogihara, Tokujo, Takamatsu, Kibigun, Okayamaken, Japan.
Oppen, William A., Stoneham, Mass.
Paschka, Hubert, Armstrong Cork Co., Pittsburgh, Pa.
Pascoe, Charles F., Villa Viau Viauville, Montreal, Canada.
Patch, Nathaniel K. B., care Lumen Bearing Co., Buffalo, New York.
Pearce, Leslie Orr Gibb, 3325 Armour Ave., Chicago, Ill.
Pedusen, Aksel M., 39 Niles St., Hartford, Connecticut.
Pelc, T., 2740 Avers Ave., Chicago, Illinois.
Pelofsky, Julius, Sulsberger and Sons, Kansas City, Kansas.
Pelton, Harold A., care of Union Oil Co. of California, Avila, San Luis
Obispo County, California.
Pensel, George R., 129 Milk St., Fitchburg, Massachusetts.
Perlstein, Harris, 5912 Calumet Ave., Chicago, Illinois.
Perlzweig, William A., 437 West 59th St., Laboratory of Physiological
Chemistry, New York City.
Peters, Frazier F., 227 West 99th St., New York City.
Pitman, Earle Carver, 29 Matthews Hall, Cambridge, Mass.
Poole, Charles R., care of Frost Gear and Machinery Co., Jackson,
Michigan.
Postma, George E., 201 South Dithridge St., Pittsburgh, Pa.
Prasil, A., 1009 Springfield Ave., Urbana, Illinois.
Prince, A. W., Jackson, Tennessee.
Quinn, Elton L., Bagdad, Florida.
Readio, Jr., James H., New Bedford Gas Co., New Bedford, Mass.
Reedy, J. H., 56 Lake Place, New Haven, Connecticut.
Roberts, Edward N., 1015 Grand Ave., Laramie, Wyoming.
Robinson, Reginald H., Science Hall, Corvallis, Oregon.
Rockwood, R. H., 83 City Hall, St. Paul, Minnesota.
Romaine, E. V., 1361 Island Ave., Milwaukee, Wisconsin.
Rosenfeld, Edwin N., 421 East 51st St., New York City.
Roth, E. K., 214 Cascadilla Park, Ithaca, New York.
Russell, Robbins, 1109 Monad Ave., Jacksonville, Illinois.
Salter, Robert M., 70 West Woodruff Ave., Columbus, Ohio.
Sankowsky, Nikolai A., 6 Nemetskaya, Moscow, Russia.
Schlichting, Jr., Louis, 67 West 8th St., Bayonne, New Jersey.
Schliep, Ernest, 224½-7 Copp Bldg., Los Angeles, California.
Schmidt, Edward, 75 West Tenth Ave., Columbus, Ohio.
Schnitzspahn, Philip T., 18 St. John's Place, Buffalo, New York.
Schommer, John J., 4338 Greenview Ave., Chicago, Illinois.
Scott, Ernest L., 437 West 59th St., New York City.
Seeley, M. J., 217 Science Hall, Corvallis, Oregon.
Seth, Erik G., 820 North East St., Indianapolis, Indiana.
Shafor, Ralph W., 218 East 17th Ave., Columbus, Ohio.
Shaw, Joseph B., 153 Merrimac St., Pittsburgh, Pa.
Shaw, Merle Branard, Park St., Orono, Maine.
Shulmyer, Charles J., 291 California Ave., Providence, Rhode Island.
Skinner, Fred V., Laramie, Wyoming.
Smith, Leslie D., 126 Chemistry Building, Urbana, Illinois.
Solomons, Jr., I. A., 2315 Bull St., Savannah, Ga.
Spriestersbach, David O., 725 So. Robert St., St. Paul, Minnesota.
Stansel, Thomas B., 408 Stewart Ave., Ithaca, New York.
Steele, Franklin H., 47 Institute Road, Worcester, Mass.

Stephens, Walter J., Box 148, Iowa City, Iowa.
Stevenson, 3rd, Hugh C., 527 East North St., Pottsville, Pa.
Stickley, J. P., South Carolina Cotton Oil Co., Columbia, South Carolina.
Swan, John C., Marietta, Ohio.
Swanstrom, Carl A., 40 West 65th St., New York City.
Syron, Charles L., 208 East 10th St., Dallas, Texas.
Taber, Jr., George Hathaway, care of Kentucky Solvay Co., Ashland, Kentucky.
Taylor, Clinton B., 70 Hackley St., Bridgeport, Connecticut.
Taylor, Cyril S., Bureau of Standards, Washington, D. C.
Taylor, William, 151 West 140th St., New York City.
Thomas, Lawrence M., 235 Washington Ave., Bay City, Michigan.
Thompson, Harry W., 1340 Girard St., N. W., Washington, D. C.
Thorolf, Valentine, Larkin Co , Buffalo, New York.
Tinkler, Loyal G., 104 Harvard Place, Ithaca, New York.
Tobor, J. Atwood, Corinna, Maine.
Towle, Theodore W., Suinsan Gardens, Shangai, China
Tripler, Guy, Wm. C. Robinson and Son Co., Coraopolis. Pa.
Ulrich, William H., 462 14th St., Brooklyn, New York.
van der Scheer, J., 166 Remsen St., Brooklyn, New York.
Vandiver, B. A., University of South Carolina, Columbia, South Carolina.
Vassian, J. G., Columbia Conserve Company, Indianapolis, Indiana.
Vibrans, Frank C., 57 Wendell St., Cambridge, Mass.
Waldie, George McLeod, State Infirmary, Tewksbury, Mass.
Walker, J. R., Point Loma, California.
Wallace, Edwin S., University of Mississippi, Oxford, Mississippi.
Waller, Coleman B., Spartanburg, South Carolina.
Ward, Louis E., 122 Somerset St., Rumford, Maine.
Washington, Henry S., Geophysical Lab., Washington, D. C.
Waxman, Harold M., 3413 Grapevine St., Indiana Harbor, Indiana.
Weber, Lothar E., 729 Boylston St., Boston, Mass.
Wescott, Jr., Josiah P., care of Atlas Chemical Co., Newtonville, Mass.
Wessling, Miss Hannah L., Bureau of Chemistry, Washington, D. C.
Whaley, Francis A., 3 Central Ave., Ithaca, New York.
White, Arthur J., 3417 Race St., Philadelphia, Pa.
Whittington, J. A., 48 West 34th St., Chicago, Illinois.
Wilson, Stansbury, M. Baugh Chemical Co., Canton, Baltimore, Maryland.
Winter, H. O., 6140 Vernon Ave., Chicago, Illinois.
Wishinck, I., Mokena, Illinois.
Woodruff, Frank O., 88 Broad St., Food Inspection Laboratory, Boston, Mass.
Wooluer, Jr., Adolph, 439 Mass. Ave., Peoria, Illinois.
Wrisley, George A., 601 Healey Ave., Champaign, Illinois.
Yonkman, William, 10850 Wentworth Ave., Chicago, Illinois.
Zavertnik, Joseph, 2871 So. Crawford Ave., Chicago, Illinois.
Zieget, Jr., Conrad, 422 West Franklin St., Baltimore, Maryland.
Zinkheisen, Oscar T., 135 William St., New York City.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

WESTERN NEW YORK SECTION.

The November meeting was held at Niagara Falls, N. Y., on November 24th. Dr. Maximilian Toch addressed the Section on "Chemical Engineering New and Old," giving lantern illustrations. At the close of the session, the members were entertained by the International Acheson Graphite Co.

The December meeting was held at the University of Buffalo, on Dec. 17th. Papers were read by Mr. Henry Bowen on "Some Features of the Acid Industry in the United States," and by Mr. E. M. Sergeant on "Potash."

The January meeting was held January 13th at Canasius College. Mr. H. E. Howe, of Rochester, spoke on "Optical Glass" and "The Projection of Spectra," with lantern illustrations.

WALTER WALLACE, *Secretary.*

OREGON SECTION.

At the annual meeting of the Oregon Section, held Saturday, November 29th, the following officers were elected for the coming year:

President, Prof. O. F. Stafford, University of Oregon, Eugene, Ore.; Vice-President, Prof. Wm. C. Morgan, Reed College, Portland; Secretary, F. A. Olmsted, Oregon City; Councilor, A. L. Knisely, 310 Worcester Bldg., Portland.

Following the business session the following papers were presented: "Fertilizer," by C. E. Travillion, and "Chemical Control of a Lead Smelter," by V. P. Edwardes.

F. A. OLMSTED, *Secretary.*

PUGET SOUND SECTION.

The annual business meeting and election of officers of the Section was held at the University of Washington, November 29th. The following officers were elected for 1914:

Chairman, C. E. Bogardus; Vice-Chairman, Dr. H. K. Benson; Secretary, Ray W. Clough; Treasurer, E. A. Dieterle; Councilor, Dr. H. G. Byers.

Ladies were invited and after the business meeting, with Dr. W. M. Dehn as floor manager and an old fashioned "fiddler" to furnish the music, everyone joined in the dances of fifty years ago, quadrilles, the Virginia Reel, etc., that our grandfathers enjoyed. None of the modern dances were allowed.

RAY W. CLOUGH, *Secretary.*

COLUMBUS SECTION.

At the December meeting of the Section the following officers were elected for the ensuing year:

President, C. W. Foulk; Vice-President, L. A. Weinland; Councilor, William Lloyd Evans; Secretary-Treasurer, D. J. Demorest.

<div align="right">D J Demorest, *Secretary*.</div>

PITTSBURGH SECTION.

At the December meeting the Section elected the following officers for the year 1914:

Chairman, Dr. R. F. Bacon; Vice-Chairman, A. C. Fieldner; Secretary, C. G. Storm, Bureau of Mines; Treasurer, G. A. Burrell; Councilors, James O. Handy, F. C. Phillips, J. H. James.

<div align="right">Horace C Porter, *Acting Secretary*.</div>

NEW YORK SECTION.

At the December 12th meeting of the Section the following councilors were elected:

Chas. Baskerville, T. J. Parker, Allen Rogers, W. H. Nichols, J. Merritt Matthews, C. M. Joyce, C. G. Fink, A. C. Langmuir, H. R. Moody, F. J. Metzger, B. C. Hesse.

The fourth regular meeting was held in Rumford Hall, January 9th. C. E. Kenneth Mees, of the Eastman Kodak Company, spoke on "The Methods of Photographic Research· An Account of the New Research Laboratory of the Eastman Kodak Company at Rochester, and of the Work which it is Intended to do there."

<div align="right">C M. Joyce, *Secretary*.</div>

MAINE SECTION.

The annual meeting of the Section was held in Orono, December 12th. Officers for the coming year were elected as follows:

President, Martin L. Griffin; Vice-President, H. D. Evans; Councilor, R. H. McKee; Secretary and Treasurer, H. H. Hanson.

Following the election an interesting address was given by Doctor Evans, Director of State Laboratory of Hygiene upon the Water Supplies of Maine.

<div align="right">H H Hanson, *Secretary*</div>

INDIANA SECTION.

The Section was addressed by Dr. J. H. Mathews, of the University of Wisconsin, on "Color Photography," at Shortridge High School, December 13, 1913.

The Section met at the Chamber of Commerce, on Friday, January 9th, and was addressed by Dr. H. C. Peffer, Professor of Chemical Engineering in Purdue University, on "The Aluminum Industry."

<div align="right">A B Davis, *Secretary*.</div>

NORTHERN INTERMOUNTAIN SECTION.

The Section held a meeting at Moscow on Saturday, December 13th, where Prof. Richard S. McCaffrey addressed the Section on "The Electric Furnace Smelting of Lead-Zinc Ores," and Prof. Geo. A. Olson on "Increasing the Nitrogen Content of Wheat."

<div align="right">Geo. A. Olson, *Secretary*.</div>

ROCHESTER SECTION.

The Section met at the University of Rochester on Monday, December 15th. Dr. L. E. Shepard, of the Eastman Kodak Company, presented a very able paper on the "The Scope of Colloidal Chemistry."

On Monday, January 12th, Prof. A. H. White, of the University of Michigan, addressed the Academy of Science on "Under What Conditions is Concrete a Safe Building Material?" Members of the Rochester Section were invited.   WM. H. EARLE, Secretary

SOUTHERN CALIFORNIA SECTION.

The 'Chamber of Mines and Oil, the Southern California Section of the American Institute of Mining Engineers, the Sierra Madre Club and this Section joined in an informal dinner at the Sierra Madre Club, Tuesday, December 16th, in honor of Dr. Irving C. Allen, Petroleum Chemist of the Bureau of Mines. Dr. Allen spoke in regard to the oil work of the Bureau and also in regard to the petroleum exhibit at the Panama-Pacific Exposition.

The regular December meeting of this Section was held jointly with the Chamber of Mines and Oil and the Southern California Section of the American Institute of Mining Engineers, December 19th. The following officers were elected for 1914: President, Richard S. Curtiss; Vice-President, Erwin H. Miller; Secretary-Treasurer, Walter L. Jordan; Councilor, Walter A. Schmidt. The following program was presented: "Antimony; its Ores, Metallurgy and Uses," by Mr. L. C. Mott; "The Technological and Coöperative Petroleum Work of the Bureau of Mines," by Dr. Irving C. Allen.

The regular January meeting of the Section was held January 16, 1914, preceded by dinner at six o'clock. A special menu was provided, which was "Chemical Dutch." The following program was presented: "The Universal Equilibrium," by Dr. Elbert E. Chandler, Occidental College; "The Sanitation Service of Porto Rico," by Mr. H. J. Lucas, Throop College of Technology.   WALTER L. JORDAN, Secretary

UNIVERSITY OF ILLINOIS SECTION.

The December meeting of the Section was held at the University of Illinois, December 16th.

Mr. A. V. H. Mory, Chief Chemist for Sears, Roebuck and Company of Chicago, spoke upon the subject "The Chemist, a Growing Factor in Merchandising."

The officers elected for 1914 were as follows: Chairman, S. W. Parr; Vice-Chairman, Geo. McPhail Smith; Councilor, E. Bartow; Treasurer, Dr. A. McInnes; Secretary, D. F. McFarland.   D F McFARLAND, Secretary

CINCINNATI SECTION.

At the 189th regular meeting of the Section, held December 17th,

the following officers were elected to serve for the year 1914: President, F. W. Weissmann; Vice-Presidents, Clarence Bahlmann, Richard Lord; Secretary, Stephan J. Hauser, 1623 Maple Ave., College Hill, O.; Executive Committee, W. R. Fleming, C. P. Long, B. R. Hart, Councilors, L. W. Jones, Archibald Campbell.   STEPHAN J. HAUSER, *Secretary*

RHODE ISLAND SECTION.

The December meeting of the Section was held in Providence, on Thursday evening, December 18th.

Mr. Charles E. Swett addressed the Section on "The Alkali Lakes of the Southwestern Desert."

Preceding the meeting, a dinner was served in the same room.
                                                NORMAN E. HOLT, *Secretary*

UNIVERSITY OF MICHIGAN SECTION.

The December meeting was held December 18th, in the Chemistry Building. A paper was presented by W. G. Smeaton on "Some Problems Relating to Metal Surfaces."   W. G. SMEATON, *Secretary.*

DETROIT SECTION.

The regular meeting of the Detroit chemists occurred on December 19th, in the Stevens Building.

Mr. Abram T. Baldwin, President and General Manager of the Precision Instrument Company, Detroit, gave a paper on "Calorimetry of Illuminating and Producer Gases" (lantern slides).
                                                ROBERT T. HARRIS, *Secretary.*

NORTHEASTERN SECTION.

The Northeastern Section held its annual meeting at the Engineers' Club, December 19th. The following officers for the ensuing year were elected: President, J. Russell Marble; Vice-President, Otto Folin; Treasurer, Hermann C. Lythgoe· Secretary, Grinnell Jones; Executive Committee, H. J. Skinner, M. H. Clark, E. Weintraub, R. E. Gegenheimer, B. S. Merigold; Councilors, H. P. Talbot, J. F. Norris, W. L. Jennings, R. S. Weston.

The address of the evening was upon "Nitrogen-filled Lamps," by Mr. J. Orange, of the General Electric Company.   W. K. LEWIS, *Secretary.*

LOUISIANA SECTION.

The seventy-second meeting was held at the Louisiana State Museum, December 19th. Dr. F. W. Zerban spoke on "The German Potash Mines, Illustrated Lecture."   J. HEATH LEWIS, *Secretary.*

WASHINGTON SECTION.

The 233rd meeting was held in the Assembly Hall of the Cosmos Club December 22nd.

Professor Earle B. Phelps, of the Hygienic Laboratory, lectured on "Recent Advances in Sewage Chemistry."

The 234th meeting was held on January 8th.

The program consisted of addresses by L. F. Kebler, of the Bureau of Chemistry, on "Chemical Investigations in Tablet Medication," and Wirt Tassin, Consulting Chemist, on "Metallography Applied to Inspection," illustrated by lantern slides.   ROBERT B SOSMAN, *Secretary*

CALIFORNIA SECTION.

On December 29th, in the Chamber of Commerce, Irving C. Allen, of the United States Bureau of Mines, addressed the oil men, and others interested, on the relation of the work of the Bureau to the petroleum industry and also its connection with the American Petroleum Society.
                                        BRYANT S DRAKE, *Secretary*

ALABAMA SECTION AND GEORGIA SECTION.

These two sections met jointly on Thursday, January 1, 1914, at Atlanta. The following papers were given: W. V. Metcalf, Fisk University, "The Cause of Osmotic Pressure." Charles L. Parsons, Bureau of Mines, "Some Possibilities of Georgia Clays." A. M. Muckenfuss, University of Mississippi, "Permeability Measurements as an Aid in Proximate Organic Analysis." Charles P. Fox, Akron, Ohio, "Rubber Substitute from the Holly." Morris O. Gottleib, Houston, Texas, "Mexican Petroleums." W. P. Heath, Atlanta, Georgia, "Manufacture of Carbon Dioxide, and its Incorporation into Water." G. P. Shingler, Emory College, Oxford, Ga., "Walnut Stain in the Killing of Fish." Ray C. Werner, Georgia State Board of Health, Atlanta, Georgia, "Sanitary Water Analysis in Relation to Public Health. "C. A. Wells, Experiment, Ga., "Cotton Seed Meal as a Possible Food for Man." R. K. Duncan, Mellon Inst., Pittsburgh, Pa., "Industrial Fellowship." J. S. Brogdon, Atlanta, Georgia, "Chemistry in Relation to the Development of the Fertilizer Industry." C. L. Hare, Auburn, Alabama, "Studies of the Chemical Composition of Cotton Seed." B. B. Ross, State Chemist of Alabama, "Occurrence and Composition of Some Alabama Phosphates." T. E. Keitt, Clemson College, S. C., "An Incompatability in Fertilizer Mixing," "Two Partially Compensating Sources of Error in the Official Method for Determining Potash."

WALLACE L. CALDWELL, *Secretary*, Alabama Section.
J S BROGDON, *Secretary*, Georgia Section.

KANSAS CITY SECTION.

The 98th regular meeting was held in the University of Kansas, January 10th.

The following program was presented: "The Standardization of Rennin," by Prof. L. D. Havenhill. "The Utilization of Wood Products," by Prof. O. A. Beath. "Some Industrial Applications of Physical Chemistry," by Prof. P. V. Faragher.   W. B. SMITH, *Secretary*.

CONNECTICUT VALLEY SECTION.

The 21st regular meeting of the Section was held in Hartford, January 10th. Following a dinner, the meeting was held in Jewell Hall, where W. R. Hulburt, of The Goldschmidt Thermit Company, delivered an illustrated lecture on the Thermit process. The lecture was illustrated by both moving picture and stereopticon views.   F. P. GILLIGAN, *Secretary.*

CLEVELAND SECTION.

The Section held its meeting at the City Club, January 12th.

Dr. H. L. Rockwood, Medical Inspector of the Ohio State Board of Health, addressed the Section on "Some Phases of Occupational Diseases."

On December 15th the following officers were elected: Chairman, Mr. C. B. Murray; Secretary-Treasurer, Mr. W. R. Eipper; Managers, Mr. E. C. Holton, Mr. A. T. Baldwin; Councilors, Mr. L. C. Drefahl, Dr. A. W. Smith.   W. R. EIPPER, *Secretary.*

ST. LOUIS SECTION.

The January meeting was held on Monday evening, January 12th, at the Missouri Athletic Club.

Dr. L. F. Nickell, of Washington University, presented a paper on "Amino Camphoric Acids."

A dinner was served at 7 P.M.

At the annual meeting the officers elected for 1914 were: Dr. Leroy McMaster, President; A. C. Boylston, Vice-President; E. J. Ericson, Treasurer; Geo. Lang, Jr., Secretary; W. F. Monfort, Councilor.   GEO. LANG, JR., *Secretary.*

LEXINGTON SECTION.

The Section held its thirteenth regular meeting in the Kentucky Agricultural Experiment Station, on January 14th. The program was as follows: "The Occurrence of Manganese in the Colored Portions of Plants and a Short Method for its Determination," by J. S. McHargue. "The Evidence of the Action of Oxydases within the Growing Plant," by G. D. Buckner.   G DAVIS BUCKNER, *Secretary.*

NASHVILLE SECTION.

The 22nd meeting of the Section was held in Vanderbilt University, on Friday, January 16th. The program included the following paper: "The Production of Anti-sheep Amboceptor in Rabbits," by Dr. Herman Spitz.   EUGENE G. GRAB, *Secretary.*

CHICAGO SECTION.

The January meeting of the Section was held at the Hotel Sherman, January 16th. The subject of the evening was an informal illustrated talk on "Atmospheric Pollution," by Mr. William Hoskins, assisted by Mr. H. V. Main.   D. K. FRENCH, *Secretary.*

WOLCOTT GIBBS FUND FOR CHEMICAL RESEARCH.

The Trustees of the Wolcott Gibbs Fund for Chemical Research are prepared to receive applications for grants of moderate size from the income of the Fund, which should be addressed to Professor C. L. Jackson, Cambridge, Mass., and should contain a sufficient account of the proposed work to allow the Trustees to judge its importance and chances of success. The applicant, if not a chemist of established reputation, should send references to papers published by him, and a statement of his chemical training with the names and addresses of some of his teachers.

<div align="right">C. L. JACKSON, Chairman of the Board of Trustees.</div>

SPRING MEETING

The forty-ninth General Meeting of the American Chemical Society will be held in Cincinnati, Ohio, April 8 to 11, 1914. The officers of the local section are: President, F. W. Weissmann, 2900 Vine St., Cincinnati, Ohio, and Secretary, Stephen J. Hauser, 1623 Maple Avenue, College Hill, Cincinnati, Ohio. A more complete statement of the meeting should be looked for in the March Journals. The titles of papers should be sent to the Secretary, Charles L. Parsons, Box 505, Washington, D. C.

The committees for the Cincinnati Section for the Spring Meeting are as follows:

Executive Committee.—Frederick W. Weissmann, Chairman; S. J. Hauser, Secretary; Archibald Campbell, Gordon Farnham, C. T. P. Fennel, J. W. Ellms, R. Lord, F. C. Broeman, L. W. Jones, John Uri Lloyd.

Finance Committee.—Archibald Campbell, Chairman; G. Merrell, O. Diechmann.

Committee on Transportation and Excursions.—Gordon Farnham, Chairman; W. R. Fleming, R. A. Proctor, F. O. Clements.

Committee on Press, Publicity and Printing.—C. T. P. Fennel, Chairman; M. B. Graff, J. C. Hartzell.

Committee on Reception and Registration.—J. W. Ellms, Chairman; H. E. Newman, F. E. Dixon, F. Homburg.

Ladies Reception Committee.—Mrs. J. W. Ellms, Chairman; Mrs. F. W. Weissmann, Mrs. S. J. Hauser, Mrs. A. Campbell, Mrs. C. T. P. Fennel, Mrs. R. Lord, Mrs. F. C. Broeman, Mrs. L. W. Jones, Mrs. A. Springer, Mrs. J. U. Lloyd.

Entertainment Committee.—Richard Lord, Chairman; C. Bahlmann, C. Von Egloffstein, E. K. Files.

Smoker Committee.—F. C. Broeman, Chairman; E. B. Reemelin, R. Hochstetter, J. Greyer, G. K. Elliot.

Banquet Committee.—L. W. Jones, Chairman; C. P. Long, H. S. Fry, L. Forst.

Committee on Meeting Places.—John Uri Lloyd, Chairman; A. Springer, S. Waldbott, H. M. Goettsch, P. H. Smyth.

Proceedings.

CINCINNATI MEETING.

The date of the Cincinnati meeting has been changed from April 8th to 11th to April 7th to 10th. Advance detail of the meeting will be found in the March *Journal of Industrial and Engineering Chemistry*.

COUNCIL.

MEMBERS ELECTED BETWEEN JANUARY 15TH ANT FEBRUARY 15TH, 1914.

Ashby, James Chester, South Bethlehem, Pa.
Appleman, C. O., College Park, Maryland.
Anderegg, Frederick O., Conant 36 A, Cambridge, Mass.
Adams, W. C., 604 Green Ave., Champaign, Ill.
Ballantyne, James Cowleg, 355 Oakland Ave., Pittsburgh, Pa.
Bartholomew, Frank J., Hotel Snyder, Palmerton, Pa.
Bartlett, Edwin Rice, Hooker Electrochemical Co., Niagara Falls, N. Y.
Bates, Joseph Sumner, 51 Prospect St., New Haven, Conn.
Behrman, A. S., P. O. Box 616, Kentucky State University, Lexington, Ky.
Bennett, J. L., Independent Powder Co., Carthage, Missouri.
Bender, Joseph Charles, 216 Cascadilla Park, Ithaca, N. Y.
Bishop, George M., 316 N. Lake St., Madison, Wisconsin.
Bliss, Roland R., 268 Littleton St., West LaFayette, Indiana.
Bragg, Thomas, Alabama Polytechnic Institute, Auburn, Alabama.
Bramson, Charles, Provident Chemical Works, 8011 Idaho Ave., St. Louis, Mo.
Brierley, John R., 432 West St., Brooklyn, New York (Sta. "Y")
Brophy, Oscar, 1919 North 12th St., Philadelphia, Pa.
Brown, D. I., No. 2 Alger St Greenfield, Pittsburgh, Pa.
Browne, Frederick L., 201 Williams St., Ithaca, New York.
Bulkley, Oscar S., 45 W. Mohawk St., Buffalo, New York.
Burdick, E. C., 307 East St Clair St., Indianapolis, Indiana.
Burgard, Howard A., 600 University Aye., Ithaca, New York.
Burns, Charles H., 316 Huntington Ave., Boston, Mass.
Cave, Gordon R., 219 Manning St., Hillsdale, Mich.
Chaney, N. K., 1614 Wyandotte Ave., Lakewood, Ohio.
Chapin, Robert M., Biochemical Division, Bureau of Animal Industry, Department of Agriculture, Washington, D. C.
Chase, Wallace S., 1430 W. 116th St., Cleveland, Ohio.
Clark, John W., West Durham, North Carolina.
Connolly, Gerald C., 1116 N. Eutaw St., Baltimore, Maryland.
Cooke, Harry, 528 North 15th St., Philadelphia, Pa.
Cox, H. L., Box 402, Chapel Hill, North Carolina.
Cragin, Harold P., 205 Rugby Road, Brooklyn, New York.
Craig, R. Sewell, 2121 North Calvert St., Baltimore, Md.
Crossley, Thomas Linsey, 318 Sagauchetiere St., W., Montreal, Canada.
Curtis, Philip C., Sayles Bleachery, Saylesville, Rhode Island.

Cushman, O. E., Vermillion, South Dakota.
Dickson, John B., Ohio State University, Columbus, Ohio.
Doerner, Henry A., Colorado Agricultural College, Fort Collins, Colo.
Doggett, Charles S., Clemson College, South Carolina.
Donaldson, Elmer D., 547 Grant St., Buffalo, New York.
Eckler, Charles R., 335 Northern Ave., Indianapolis, Indiana.
Edwards, V. C., Box 578, Chapel Hill, North Carolina.
, Engel, Karl, 1302 E. 2nd St., Ottumwa, Iowa.
Erswell, Charles S., Theta Chi House, Orono, Maine.
Ewing, Clare O., 1736 G St., N. W., Washington, D. C.
Fay, J. T., Clemson College, South Carolina.
Fenner, Benjamin C., 775 St. Johns Place, Brooklyn, New York.
Fentress, J. H., Canadian Explosives, Ltd., Nanaimo, British Columbia,
Canada.
Fetzer, Lewis William, 1700 Lawrence St., N. E., Washington, D. C.
Fleece, C. L., Graduate College, Princeton, N. J.
Flint, H. A., Solvay Process Co., Syracuse, New York.
Flume, A. J., Box 247, Chapel Hill, North Carolina.
Galpin, S. L., Dept. of Geology and Mining, Iowa State College, Ames,
Iowa.
Ganachean, James, 1439 North Johnson St., New Orleans, La.
Gardner, H. A., Asst. Director, Institute of Industrial Research, Wash-
ington, D. C.
Gerth, C. R., Theta Ki House, State College, Pa.
Glaive, August F., P. O. Box 396, San Francisco, California.
Goldstein, Milton M., 3346 Holmes Ave., S., Minneapolis, Minn.
Graham, Joseph B., 32 Summit St., Chestnut Hill, Pa.
Greenlaw, Frank Murray, 29 Mann Ave., Newport, R. I.
Grüse, W. A., 409 Park Ave., Baltimore, Maryland.
Gulick, Addison, Univ. of Missouri, Columbia, Mo.
Gygi, Paul Y., 7709 West Dennison Ave., Cleveland, Ohio.
Hackh, Ingo, The von Ruck Research Lab., Asheville, N. C.
Hamilton, Paul S., Diamond Crystal Salt Co., St. Clair, Michigan.
Harding, Edwin R., 6147 Kimbark Ave., Chicago, Ill.
Hartman, Ernest F., 182 Franklin St., New York City.
Hawes, E. B., Acacia House, W. 8th Ave., Columbus, Ohio.
Henkel, Paul L. H. H., 130 Sycamore St., Somerville, Mass.
Hinde, Charles, City Chemist, City Hall, Vancouver, British Columbia,
Canada.
Hinshaw, George, 971 North Main St., Pontiac, Ill.
Hjost, Axel M., 1005 S. Wright St., Champaign, Ill.
Hohman, Arthur, St. Joseph's College, Philadelphia, Pa.
Holloway, Percy E. P., 132 Walnut St., Everett, Mass.
Hornaday, F. A., 3509 14th St., N. W., Washington, D. C.
Huber, Harold V., 1140 Wightman St., Pittsburgh, Pa.
Howard, Norman Joseph, Department of Health, City Hall, Toronto,
Can.
Huey, H. I., 96 Chapel St., Saylesville, R. I.
Hummell, Robert C., 139 W. 9th Ave., Columbus, Ohio.
Inman, C. F., Clemson College, South Carolina.
James, L. H., 71 Harper Ave., Detroit, Mich.
Johnston, Angus, The Rookery, Chicago, Ill.

Johnson, Julius E., Box 178, University Park, Colorado.
Jones, Mary Ethel, 100 North 5th St., Alhambra, California.
Joyce, A. Willard, Chem. Lab., Lehigh Univ., South Bethlehem, Pa.
Kahlaw, Thomas J., 515 N. Frances St., Madison, Wisconsin.
Kahn, Sidney, 47 Franklin Ave., Saranac Lake, New York.
Keegel, Anthony, Kroma Color Co., Sandusky, Ohio.
Kellogg, E. H., Station A., Ames, Iowa.
Kendall, James, Chemistry Dept., Columbia Univ., New York City.
Kintner, Edward, Manchester College, North Manchester, Indiana.
Klinger, Harry W., Box 316, State College, Pa. .
Kohler, Herbert Valbrath, 702 Yale Station, New Haven, Conn.
Kramer, Benjamin J., 232 Henry St., New York City.
Lachmund, Bruno, 376 22nd St., Milwaukee, Wisconsin.   .
Ladd, R. M., 639 W. 59th St., Kansas City, Missouri.
Lamb, Newton, 700 East Court St., Flint, Mich.
Lane, Gerould T., B. D. Rising Paper Co., Housatonic, Mass.
Lang, Walter W., 33 Fairview St., Roslindale, Mass.
Larson, Robert D., 9953 Ave. J., Chicago, Ill.
Lawson, C. E., 1117 Ewing St., Indianapolis, Indiana.
Leadbeater, W. R., Dominion Sugar Co., Wallaceburg, Ontario.
LeMaistre, F., Ridley Park, Pa.
Lippert, Jr., Otto C. F., 1601 Freeman Ave., Cincinnati, Ohio.
Loebenberg, Alfred, 122^1/$_2$ Elm St., Elizabeth, N. J.
Lucas, James B., Blacksburg, Va.
Mahony, Mary Isabelle, Trinity College, Washington, D. C.
Maltauer, Frank, 3357 Woodford Ave., Pleasant Ridge, Cincinnati, O.
Mangold, Alfred C., 105 North 11th St., Brooklyn, New York.
Mansfield, Arthur T., 505 4th St., LaSalle, Ill.
Manso, Walter A., 739 River St., Troy, New York.
McCloud, John Lansford, 900 Third St., Detroit, Mich.
McClure, George M., 1248 Harrison Ave., Columbus, Ohio.
McCullock, Leon, 455 Biddle Ave., Wilkinsburg, Pa.
McNeil, C. Perkins, Ohio St ite University, Columbus, Ohio.
McQueen, Stuart A., Portland Pure Milk and Cream Co., 3rd and
Hoyt Sts., Portland, Oregon.
Michael, Arthur, 219 Parker St , Newton Centre, Mass
Michael, John A., Box 75, Hartley Hall, Columbia Univ., New York City.
Minges, G. A., 145 Pike Ave., Station A, Ames, Iowa.
Morris, J. Lucien, 121 St. Stephen St., Boston, Mass.
Morrison, J. D., Highmore, South Dakota.   '
Moss, Harold R., Sunnyvale, California.
Müller, John, The Federal Distilling Co., Baltimore, Md.
Neave, Arthur S., 461 Considine Ave., Cincinnati, Ohio.
Nessenthaler, Frank G., 220 W. 3rd St., Chester, Pa.
Netoffsky, Wm., Forestry Department, Mont Alto, Pa.
Newman, P. J., 914 Leavenworth St., Manhattan, Kansas.
North, C. Olin, 9 Mawhinney St., Pittsburgh, Pa.
Okell, Stanley Allen, care West Virginia Pulp and Paper Co., 521 W.
23rd St., New York City.
Olmstead, L. B., Bureau of Soils, Washington, D. C.
Palkin, Samuel, 1215 Eye St., N. W., Washington, D. C.
Parkinson, George E., 147 Beulah Avenue, Zanesville, Ohio.

Peterjohn, Alvin C., West Park, Cuyahoga Co., Ohio.
Pieper, Ernest J., 2 W. Erdman Ave., Baltimore, Md.
Pleiss, Paul, 50 Church St., New York City.
Powders, J. A., Mt. Prospect Lab., Department of Water Supply, Brooklyn, N. Y.
Pratt, Stafford Henry, Star Rubber Co., South Akron, Ohio.
Probeck, Edwin J., 1368 East 91st St., Cleveland, Ohio.
Race, Joseph, Civic Laboratories, Ottawa, Canada.
Rathbun, Harry B., 41 Holmes Ave., Waterbury, Conn.
Rauber, Benjamin T., 40 Rutland Square, Boston, Mass.
Raynolds, Russell P., American Smelting and Refining Co., 1st National Bank Building, Denver, Colo.
Reid, Howard E., Siegfried, Pa.
Rhea, H. M., 511 Bureau of Chemistry, Washington, D. C.
Richter, George, 21 Clary St., Cambridge, Mass.
Riordan, Joseph A., 26 South 4th St., Duquesne, Pa.
Riticor, Charles C., Lexington, Virginia.
Ritter, Ralph B., 730 S. Karlov Ave., Chicago, Ill.
Robertson, James D., 1403 Syndicate Trust Bldg., St. Louis, Mo.
Robison, Clinton S., 1360 Kenwood Park Place, Chicago, Ill.
Rost, Clayton O., University Farm, Division of Soils, St. Paul, Minn.
Rudolf, Eugene A., 726 So. Lombard Ave., Oak Park, Chicago, Ill.
Russell, D. A., Youngstown Sheet and Tube Co., Youngstown, Ohio.
Salkover, Ben, 256 Ehrman Ave., Avondale, Cincinnati, Ohio.
Salter, Frederick J., 43 Chittenden Ave., Columbus, Ohio.
Schneider, William A., 2940 Broadway, New York.
Schroth, Robert Carl, Jr., 1521 Mento Place, Columbus, Ohio.
Schuette, Adolph J., 3950 North Ashland Ave., Chicago, Ill.
Schulte, Louis, 1431 Leland Ave., Chicago, Ill.
Schwabbauer, Georg, 211 Monterose Ave., Syracuse, New York.
Selecter, I., Baton Rouge, Louisiana.
Seybert, John Edward, Eli Lilly and Co., Indianapolis, Indiana.
Shaw, John S., Pinole, California.
Sherman, A. L., Box 353, State College, Pa.
Shewade, V. Y., 825 Adams St., Gary, Indiana.
Siegmund, Harry B., 1918 Wilkins Ave., Baltimore, Maryland.
Sive, Benjamin E., 15 St. Leger Bldg., Walnut Hills, Cincinnati, Ohio.
Smith, Olin K., 511 Hartley Hall, Columbia University, New York City.
Smith, S. Hodge, Box "D," Bowmanville, Ontario, Canada.
Smyth, Douglas S., 10 Edgewood Ave., New Haven, Connecticut.
Shoddy, Arnon O., 735 Froome Ave., Winton Place, Cincinnati, Ohio.
Sporer, J. Lorenz, 38 West 75th St., New York City.
Statham, Noel, 200 5th Ave., New York City.
Stevens, R. H., 4 Marquette Apartments, 6th E. and 3rd So., Salt Lake City, Utah.
       t, Clifton O., 828 Kirby Ave., Muncie, Indiana.
         , George H., care Pacific Products Co., Port Townsend, Washington.
Struna, Stephen C., 708 Bingham St., Pittsburgh, Pa.
Sugiura, Kanematsu, Harriman Research Lab., Roosevelt Hospital, N. Y. City.
Supple, Lee F., 6152 St. Lawrence Ave., Chicago, Ill.

Sutherland, George, 4459 W. Monroe St., Chicago, Ill.
Tanis, John E., 630 S. Weadock Ave., Saginaw, Michigan.
Taylor, Royal W., 707 W. Lake St., Canton, Ohio.
Tailby, J. Allen, 368 Congress St., Boston, Mass.
Tavenner. R. W., Box 273, Crockett, California.,
Taylor, Carl A., 2 Alger St., Pittsburgh, Pa.
Taylor, E. H., 808 South Matthews Ave., Urbana, Ill.
Tchorni, David L., 1029 Currier St , Chicago, Ill.
Thatcher, Arthur Stockton, Apt. 42, 2140 N St., N. W., Washington, D. C.
Thomas, Stanley Judson, 308 W. Packer Ave., South Bethlehem, Pa.
Tietig, Chester, 1400 L. St., N. W., Washington, D. C.
Torossian, Gregory, 11014 Detroit Ave., Suite 4, Cleveland, Ohio.
Traquair, John, Ayer, Mass.
Turck, Fenton B., 428 Lafayette St., New York City.
Vandreuil. Lorenzo J., 2 Hudson St., Worcester, Mass.
Van Marle, D. J., 18 Scotland St., Orange, N. J.
Van Siclen, James V., 507 River St., Hoboken, N. J.
Viehoever, Arno, 202 11th St., S. W., Washington, D. C.
Waldbauer, Louis, 208 Williams St., Ithaca, New York.
Wales, Harold Edward, 3333 19th St., San Francisco, Calif.
Walter, Howard A., 30 South Second St., Elizabeth, N. J.
Wharton, R. L., 5018 Liberty Ave., Pittsburgh, Pa.
White, Ralph H., Oxford, Mass.
Whitney, Carrol Nathan, 127 W. 17th St., Wilmington, Del.
Whiton, Louis C., Jr., 310 W. 97th St., New York City.
Widdicombe, R. A., 5552 Lakewood Ave., Chicago, Ill.
Williams, Dean, Sigma Pi House, State College, Pa.
Williams, Joseph J., N. J. Agricultural Experiment Sta., New Brunswick, N. J.
Wolf, Maurice A., 4 Manning St., Providence, R. I.
Wright, L. E., 1545 Contant St., Lakewood, Ohio.
Wyler, Joseph, C-32 Taylor Hall, Lehigh Univ., South Bethlehem, Pa.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

LOUISIANA SECTION.

At the annual election of officers for this Section held Jan. 16th, the following were elected:

W. L. Howell, *President;* Geo. B. Taylor, *Vice-President;* J. Heath Lewis, *Sec.-Treas.;* B. P. Caldwell, *Member Exec. Comm.;* Dr. Chas. E. Coates, *Councilor.*

J. Heath Lewis, *Secretary.*

CORNELL, ROCHESTER, EASTERN AND WESTERN NEW YORK AND SYRACUSE SECTIONS.

The five New York sections held a joint meeting at Syracuse University, Syracuse, New York, on January 17th. The afternoon meeting was held

at the Bowne Hall of Chemistry at 2.30 o'clock, where, after an address of welcome by Honorable Louis Will, Mayor of Syracuse, the following papers were given: "The Use of Physical Measurements in Chemistry," by Dr. C. W. Kenneth Mees, Director of the Research Laboratories of the Eastman Kodak Company, of the Rochester Section; "Hydrogen Telluride and the Atomic Weight of Tellurium," by Dr. Ross P. Anderson of Cornell University, of the Cornell Section; "The Dissociation of Hydrogen into Atoms," by Drs. F. Langmuir and G. M. J. MacKay of the General Electric Company, Schenectady, New York, of the Eastern New York Section; "The Oxidation of Ammonia to Nitric Acid," by G. N. Terziev, of the Solvay Process Co., and "Microscopical Demonstrations with Especial Reference to the Ultramicroscope," by Dr. H. C. Cooper, of Syracuse University, of the Syracuse Section.

The Syracuse Section gave an elaborate dinner to the visiting sections in Sims Hall.

The evening meeting was held in the Auditorium at Crouse College. After an organ recital in Crouse Hall, Chancellor Day of Syracuse University spoke "A Word of Welcome." Dr. Charles P. Steinmetz, Professor in Union College and Chief Consulting Engineer of the General Electric Company of Schenectady, lectured on "Electrical Energy."

The patrons were the Brown-Lipe Chapin Co., Brown-Lipe Gear Co., General Chemical Co., Halcomb Steel Co., Merrell Soule Co., The Solvay Process Co., Straight Line Engine Co., Will and Baumer Co., Messrs. W. B. Brookfield, H. G. Carrell, E. L. French, E. S. Johnson, L. C. Jones, H. B. Kipper, and D. A. Morton.

There was an attendance of about 250 at the afternoon sessions, 150 at the dinner and 800 to 1000 at the Steinmetz evening lecture, to which Syracuse University and Syracuse Technology Club members were especially invited. Twenty-five registered from the Rochester Section. Ithaca was also especially strongly represented with good attendance from the Eastern and Western New York Sections. The meeting was therefore a thorough success.

C. F. HALE, *Secretary*, Eastern New York Section.
W. H EARLE, *Secretary*, Rochester Section.
O R OVERMAN, *Secretary*, Cornell Section
WALTER WALLACE, *Secretary*, Western New York Section
H. B. KIPPER, *Secretary*, Syracuse Section.

CORNELL SECTION.

The Section met Monday, January 19th, in Morse Hall.

Three papers were presented· "The Fractional Crystallization of the Picrates of the Rare Earths of the Didymium Group," by F. H. Rhodes. "Hydrogen Telluride and the Atomic Weight of Tellurium," by R. P. Anderson. "A New Method for the Determination of Hydrocyanic Acid and the Alkali Cyanides," by G. E. F. Lundell.

O. R. OVERMAN, *Secretary*.

WISCONSIN SECTION.

The January meeting of the Section was held in the Chemistry Building on Wednesday, Jan. 21st. Prof. David Klein gave a lecture with demonstrations on "Recent Developments in Colloid Chemistry."

The February meeting of the Section was held on Wednesday, Feb. 18th. Prof. A. S. Loevenhart presented a paper on "Certain Responses of the Animal Body to Alteration in the Rate of Oxidative Processes."

<div align="right">A. E. KOENIG, <i>Secretary.</i></div>

PITTSBURGH SECTION.

The one hundred and fourth regular meeting of the Section was held at the University of Pittsburgh, January 22nd. The address of the evening was on "Adrenaline: Its Nature and Composition," by E. R. Weidlein, Mellon Institute of Industrial Research, University of Pittsburgh.

<div align="right">C G STORM, <i>Secretary</i></div>

PHILADELPHIA SECTION.

The regular meeting of the Section was held on January 22nd, at the Engineers' Club, Philadelphia. The program consisted of the following: "The Saponins," by Carl L. Alsberg, Chief, Bureau of Chemistry, U. S. Dept. of Agriculture, Washington, D. C.; "The Chemistry of Fires and Chemicals in Fires," by Mr. Chas. A. Hexamer, of the Fire Underwriters' Association. Prof. Philip Maas, of the Central High School, exhibited a very interesting collection of liquidified gases, including many not ordinarily seen.

The February meeting of the Section was held at the Franklin Institute, Saturday, February 21st. An illustrated address on "The New Era in Chemistry," was given by Harry C. Jones, Ph.D., of Johns Hopkins University, Baltimore, Md.

<div align="right">C. S. BRINTON, <i>Secretary.</i></div>

MICHIGAN SECTION.

There was a meeting of the Section Thursday, Jan. 22nd, in the Chemistry Building. Mr. W. L. Badger addressed the Society on "The Work of the Bureau of Standards."

<div align="right">H. H WILLARD, <i>Secretary.</i></div>

EASTERN NEW YORK SECTION.

The January meeting was held at the Edison Club, Schenectady, on Friday evening, January 23rd. The program was a symposium on "Electronics and Chemistry," led by Dr. Saul Dushman, with supplementary papers by Messrs. Whitney, Coolidge and Langmuir. The meeting was preceded by a dinner.

At a meeting of the Section held on Friday, Jan. 23rd, the following officers were elected for the ensuing year: *President*, A. D. Carrier; *Vice-President*, Irving Langmuir; *Secretary-Treasurer*, William C. Arsem;

Councilor, M. A. Hunter; *Executive Committee*, A. T. Lincoln, C. F. Hale, R. C. Robinson.   C. F. HALE, *Secretary*.

UNIV. OF MISSOURI SECTION.

The forty-fifth regular meeting of the Section was held in the Physics Building, Friday, January 23rd. Prof. J. A. Gibson presented a paper on "The Consideration of Some Data on the Teaching of Chemistry in Universities."

The following officers were elected:

Dr. L. E. Wise, *Chairman;* Dr. L. D. Haigh, *Vice-Chairman;* Mr. O. C. Smith, *Secretary;* Dr. L. S. Palmer, *Treasurer;* Dr. Herman Schlundt, *Councilor.*

The forty-sixth regular meeting was held in the Chemistry Building, Friday evening, Feb. 6th. The papers of the evening were "The Acidity Determination for Soils," by C. R. Moulton and "The Hydro-chloroplatinic Acid Method Compared with the Perchloric Acid Method for Potash Determinations," by Herman Rosenthal.   O. C. SMITH, *Secretary*.

ALABAMA SECTION.

A meeting of the Section was held in the Brown Marx Building at Birmingham, Saturday, January 24th and papers read by Prof. B. B. Ross on "The Occurrence and Composition of Some Alabama Phosphates" and by Prof. C. L. Hare on "A Study of the Chemical Composition of Cotton Seed."   WALLACE L. CALDWELL, *Secretary*.

CALIFORNIA SECTION.

The seventy-fifth regular meeting of the Section was held at the University of California Club, January 24th. The paper of the evening was "Some Practical Applications of the Hydrogen Electrode," by Joel H. Hildebrand, of the University of California. A demonstration of the electrode was given and lantern slides shown in conjunction with the paper.

The meeting was preceded by a dinner.   BRYANT S DRAKE, *Secretary*

NORTH CAROLINA SECTION.

The mid-winter meeting of the Section was held Jan. 24th. The following officers were elected for the current year:

President, James M. Bell; *Vice-President,* J. W. Nowell; *Sec.-Treas.,* C. E. Bell; *Councilor,* A. S. Wheeler; *Reporters,* J. S. Downing, F. E. Carruth.

The following program was given:

Presidential address, "The Engineering Student's Need of Chemistry," by L. F. Williams; report, "Colors and Structure," by W. L. Jeffries; "The Stability of Resin Acids at Slightly Elevated Temperatures," by C. H Herty and H. L. Cox; "Studies in Nitrification," by W. A. Withers

and A. L. Field; "Phenylsemicarbazone of Tetrahydroxynaphthalene," by A. S. Wheeler and V. C. Edwards; "Neutral Solutions of Ammonium Citrate," by J. M. Bell; "A Study of Dammar Resin," by C. H. Herty and C. B. Carter; "Bromination of β-Hydrojuglon," by A. S. Wheeler and L. B. Rhodes; "Action of Ammonia on Arsenic Iodide," by J. T. Dobbins; "Studies in Toxicity of Cotton Seed Meal," by W. A. Withers; "Frothing in Crude Fiber Determinations—A Method for Preventing It," by J. M. Pickel; "Methods of Adiabatic Colorimetry," by J. M. Bell and W. A. Rudisill; "An Electrical Contact Vapor-pressure Thermoregulator," by A. L. Field; "The Resene of Pinus Heterophylla," by C. H. Herty and V. A. Coulter; "A Volumetric Method for Arsenates," by J. M. Bell and A. J. Flume; "Report of the Rochester Meeting," by C. H. Herty.

J. K. PLUMMER, Secretary.

RHODE ISLAND SECTION.

The January meeting of the Section was held in Providence, on Thursday evening, January 29th. Dr. Norman E. Holt, of Brown University, addressed the Section on "A Study of s-Tribromphenyl Propiolic Acid."

NORMAN E. HOLT, Secretary.

DETROIT SECTION.

The regular meeting of the Section occurred on Friday evening, January 30th, in the Stevens Building. Mr. William D. Richardson, Chief Chemist of Swift and Company, Chicago, talked upon "The History and Present Status of Food Preservation."

ROBERT T. HARRIS, Secretary.

NEW HAVEN SECTION.

The annual meeting was held on Friday evening, Jan. 30th, at the Graduates' Club. The following officers were elected: *President*, B. W. McFarland; *Vice-President*, T. B. Johnson; *Secretary*, G. S. Jamieson; *Treasurer*, W. A. Drushel; *Councilor*, Wm. Buell.

After the election of officers, the members adjourned to the Sloan Physical Laboratory and Dr. C. E. Kenneth Mees, Director of the Research Dept., Eastman Kodak Co., Rochester, N. Y., addressed the Section upon the methods of photographic research including an account of the new research laboratory of the Eastman Kodak Co.

GEORGE S. JAMIESON, Secretary

PUGET SOUND SECTION.

. The January meeting was held at the Faculty Club House, University of Washington, January 31st. The program consisted of the following addresses: "The Present Status of the Electric Furnace in the Iron and Steel Industries," by J. H. Linton, Pacific Coast Testing Laboratory; and "Electricity in the Field of Metallurgy," by B. H. Bennett, Metallurgist, Tacoma.

RAY W. CLOUGH, Secretary.

CHICAGO SECTION.

The usual meeting was postponed until February 2nd, in order that the Section might attend the first of a series of lectures by Dr. Wolfgang Ostwald at the University of Chicago. The series continued from February 2nd to 6th.

D. K. FRENCH, *Secretary.*

ROCHESTER SECTION.

The regular meeting was held Monday, February 2nd, 1914, in the Eastman Building, University of Rochester. Mr. F. A. Lidbury, Works Manager of the Oldbury Electro-Chemical Co., of Niagara Falls, addressed the section on "Some Aspects of the Electro-Chemical Industry."

A meeting was also held Monday, February 16, 1914, in Reynold's Laboratory, University of Rochester, when Mr. J. I. Crabtree of the Eastman Kodak Company, spoke on "The Nature of Overvoltage and Its Function in Electrolysis."

WILLIAM H. EARLE, *Secretary*

NEW YORK SECTION.

The fifth regular meeting of the Section was held in conjunction with the New York Sections of the Society of Chemical Industry and the American Electro-Chemical Society, on Feb. 6, 1914.

The subject of the evening was "The Undeveloped Elements." The speakers and their titles follow:

"Opening Up the Field of Unused Elements," by Dr. Chas. Baskerville, Prof. of Chemistry, College of the City of New York; "The Present Status of Cobalt," by Dr. H. T. Kalmus, Director, Research Laboratory, School of Mines, Kingston, Ont.; "The Present Status of Boron," by Dr. E. Weintraub, Director, Research Laboratory, Gen. Electric Co., W. Lynn, Mass.; "The Present Status of Tungsten," by Dr. R. W. Moore, Research Laboratory, General Electric Co., Schenectady, N. Y.

C. M. JOYCE, *Secretary.*

CONNECTICUT VALLEY SECTION.

The twenty-second regular meeting of this Section was held in Hartford, on Saturday evening, Feb. 7, 1914, preceded by a dinner at the Hotel Bond.

Mr. H. E. Howe of the Bausch & Lomb Optical Co., delivered an illustrated lecture on the subject of "The Manufacture and Manipulation of Optical Glass."

F. P. GILLIGAN, *Secretary.*

CLEVELAND SECTION.

The regular monthly meeting was held at the City Club Rooms on February 9th, preceded by an informal dinner.

The following was the program for the evening: "Theodore William Richards—President of the Society," by H. C. Chapin of The National Carbon Co.

"Physical Chemistry in the Service of the Manufacturer—A Symposium." The leaders of the discussion were Messrs. N. K. Cheney, W. C. Moore and W. R. Mott of the National Carbon Co. and W. G. Wilcox of the Cleveland Research and Testing Laboratories.　W. R. EIPPER, *Secretary*

ST. LOUIS SECTION.

The Section met Monday, Feb. 9, 1914, at the Missouri Athletic Club.

Mr. J. Lainson Wills, F.C.S. of the Stifel Laboratory of Fermentology gave an interesting address on "American Beers from a Chemical and Biological Viewpoint."　GEO. LANG, JR., *Secretary*

WASHINGTON SECTION.

The two hundred and thirty-fifth meeting was held at the Cosmos Club, Thursday, February 12th. The following addresses were given:

"Artificial Sperrylite," by F. P. Dewey, of the Bureau of the Mint; "Potash from Kelp," illustrated, by F. K. Cameron, of the Bureau of Soils; "Note on a New Extraction Apparatus," by P. H. Walker, of the Bureau of Chemistry.　ROBERT B. SOSMAN, *Secretary.*

LEXINGTON SECTION.

The Section held its fourteenth regular meeting at the Kentucky Agricultural Experiment Station, Wednesday, February 11, 1914. The program was as follows:

"Note on a Specimen of 'Black Band' Ore from the Stearns Coal Company's Mine and on the Ratio of Calcium and Magnesium in Ferrous Carbonate Ores," by A. M. Peter; "An Indirect Separation of Calcium and Strontium and of Lithium from Sodium and Potassium," by S. D. Averitt.　G. DAVIS BUCKNER, *Secretary.*

COLUMBUS SECTION.

Dr. Wolfgang Ostwald of the University of Leipzig gave a series of lectures to the Section on the subject of Colloid Chemistry. These lectures were held Monday, Feb. 16th, Tuesday, Feb. 17th, Thursday, Feb. 19th, and Friday, Feb. 20th, at 8.00 P.M., and Friday at 5.00 P.M., all in the chemical lecture room of the Ohio State University.

The subjects of the lectures were as follows:

1. "What are Colloids? Elements of Qualitative Colloid Analysis. Formation and Preparation of Colloids." 2. "Mechanical, Optical, Electrical, Chemical Properties of Substances in the Colloid State. Classification of Colloids." 3. "Changes in the Colloid State. Internal Changes of State, Swelling, Setting, Syneresis, Adsorption, Coagulation, Peptisation." 4. "Scientific Application of Colloid Chemistry." 5. "Technical Applications of Colloid Chemistry."

Friday evening a dinner was given for Dr. Ostwald at Ohio Union on the campus.　D. J. DEMOREST, *Secretary.*

PITTSBURGH SECTION.

The one hundred and fifth regular meeting of the Section of the American Chemical Society was held in the rooms of the Engineers' Society of Western Pennsylvania, Thursday, February 19th. An illustrated paper on "By-Product Coke Ovens," was given by Wm. H. Blauvelt, Consulting Engineer, Semet-Solvay Co., Syracuse, N. Y.   C. G. STORM, *Secretary.*

KANSAS CITY SECTION.

The ninety-ninth regular meeting was held at the Y. M. C. A. Building, Kansas City, February 20, 1914. The following program was presented: "The Chemical Theory of Cancer," by Dr. A. E. Hertzler;" "First Aid to the Injured for Chemists," by Dr. W. H. Bailey. Preceding the meeting a dinner was held.   W. B. SMITH, *Secretary*

NASHVILLE SECTION.

The twenty-third meeting of the Section was held in Furman Hall of Vanderbilt University, on February 20th. E. J. Pranke spoke on "Some of the Problems of the Cyanamid Industry and their Industrial Solution."
EUGENE G. GRAB, *Secretary.*

DECEASED MEMBERS.

Chapman, D. W., 238 W. 23rd St., Chicago, January 17, 1914.

Chatfield, George F., Lawrenceville, Ill., January 8, 1914.

Jewett, Walter K., Univ. of Nebraska, Lincoln, Neb.

Robert Kennedy Duncan, Director, Melton Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., February 18, 1914.

Proceedings.

BOARD OF DIRECTORS.

The directors of the American Chemical Society met at the Chemists' Club in New York City, at 3.00 P.M., Saturday, February 28, 1914.

President T. W. Richards was in the chair, and Directors Bogert, Hallock, Love, Bigelow, Smith and Parsons were present.

It was voted: That reprints for all journals of the Society be regularly issued as standard without covers. Authors should be allowed fifty such reprints gratis. Should they desire covers, they shall pay cost therefor. For all reprints above fifty, six cents per page shall be charged for each additional fifty, which price shall cover also the cost of transportation.

It was voted: That title and reference shall both be printed on the covers of all reprints with covers.

It was voted: That the territory of the California Section of the American Chemical Society and of the Southern California Section be separated by a line drawn along the northern boundaries of San Luis Obispo, Kern, and San Bernardino Counties.

A petition having been received from twenty-two chemists, members of the American Chemical Society, located in South Carolina, for a local Section, with territory covering the State of South Carolina, it was voted that the Section be authorized and a charter granted.

A vote was passed instructing the Treasurer to place a portion of the funds now in hand on Certificates of Deposit, for short terms, in order to secure a higher rate of interest than regularly allowed.

Also, that the President and Finance Committee, after consultation with Mr. Paul M. Warburg, executor of the estate of Morris Loeb, be authorized to invest a portion of the funds now in the treasury.

It was voted: That the Secretary be instructed to issue the usual directory of the Society on or before July 1, and that the necessary funds be appropriated therefor.

It was voted: That $100 be appropriated toward the Annual Table of Physical Constants for 1914.

It was voted: That the Secretary be authorized to deposit all collections made by him with the Munsey Trust Company, Washington, D. C., such deposits to be drawn out only by the check or draft of the Treasurer of the Society.

It was voted: To continue until July 1st the salary of A. M. Patterson, with the hope that he may be able to resume work by that time.

COUNCIL.

Akers, Walter W., Santa Ana, Calif.
Albrecht, Lewis, 50 Church St., New York City.
Allen, Edwin T., 123 Hartley Hall, Columbia University, New York City.
Allen, Herbert I., Apt. 4, The Marlboro, Wilmington, Del.
Andrew, James P., 3600 Shaw Ave., Cincinnati, Ohio.
Armeling, Geo. K., 1811 Riggs Ave., Baltimore, Md.
Armstrong, George W., Engineering Experiment Station, Ames, Iowa.
Attridge, Arthur J., Central Aguirre, Porto Rico.
Bast, Rev. Victor A., St. Charles College, Cantonville, Md.
Bateman, Ray C., 244 Fayette St., Johnstown, Pa.
Bennett, H. C., Santa Ana, Calif.
Berger, Oscar, 311 Waldron St., Lafayette, Ind.
Binder, William G., Delta Tau Delta House, State College, Pa.
Blatchford, John, 333 N. Euclid Ave., Oak Park, Ill.
Bloom, Charles L., 1038 Weslev Ave., Cincinnati, Ohio.
Bohnson, Van L., State College, Pa.
Borcherdt, Frederick H., 217 North Lincoln St., Chicago, Ill.
Borden, Norman H., Box 114, Kingston, R. I.
Brenner, Ralph F., 246 Atwood St., Pittsburg, Pa.
Brown, Arthur L., 553 Mifflin St., Wilkinsburg, Pa.
Brown, F. E., High School, Fresno, Calif.
Canine, Ralph J., 1935 Sherman Ave., Evanston, Ill.
Carthaus, Wm. F., 3938 Flora Blvd., St. Louis, Mo.
Cattell, J. McKeen, Garrison-on-Hudson, N. Y.
Chiaravigho, D., via Treirso 7, Roma, Italy.
Clarke, Stanley C., 4634 N. Robey St., Chicago, Ill.
Clayton, Robert H., Manchester Oxide Co., Ltd., Manchester, England.
Colby, Lawrence W., 37 High St., Andover, Mass.
Creighton, Henry J. M., Swarthmore College, Swarthmore, Pa.
Danker, Daniel J., 73 Dean Rd., Brookline, Mass.
Darrow, Floyd L., 99 Livingston St., Brooklyn, N. Y.
Davis, Chester P., 33 Arlington St., Cambridge, Mass.
Davis, Hugh N., Canonsburgh, Pa.
Davis, S. I., 1823 Barker Ave., Lawrence, Kans.
Diehl, S. H., Rigand, Quebec, Canada.
Dill, Leslie L., 82 Grang Ave., West, Highland Park, Mich.
Donk, M. G., University of Idaho, Moscow, Idaho.
Douglas, J. Parke, Mt. Pulaski, Ill.
Drackett, P. W., 62 Pickering Bldg., Cincinnati,. Ohio.
Duncan, Robert A., 1001 Locust St., Columbia, Mo.
Eddy, George L., Bay Point, Calif.
Ezekiel, Bertram, 1270 St. Patrick Ave., Montreal, Canada.
Fehnel, J. Wm., 603 N. Main St., Bethlehem, Pa.
Frederick, Wm. J., 611 Bailey Dowell Bldg., Pittsburg, Pa.
Garretson, Thos. A., Lafayette College, Easton, Pa.
Gerstle, John, 20 Virginia Apt., Rockdale Ave., Avon, Cincinnati, Ohio
Glasgow, Ruth (Miss), Mellon Institute of Industrial Research, Pittsburg, Pa.

Godlove, Isaac H , 4330 Lindell Blvd., St Louis, Mo
Gonzales, A. T , Gramercy, La
Graf, Ernest S , 4751 Prairie Ave , Chicago, Ill
Gray, John Lathrop, East 22nd St , Bayonne, N J
Guernsey, F H , 70 Tracy St , Buffalo, N Y
Guy, James S , Decatur, Ga
Habeshian, Yeranos, 610 E Raynor Ave , Syracuse, N Y
Hall, Albert E , Box 233, Mt Lebanon, Pa
Halland, Chas J , 1220 Proctor St , Port Arthur, Texas
Hanahan, Marion L , Ten 8, Univ of South Carolina, Columbia, So Car.
Hanford, H W , Illinois State Water Survey, Urbana, Ill
Hayes, F Albert, Winslow Bros & Smith Co , Norwood, Mass
Heyroth, Francis F , 637 Hawthorne Ave , Price Hill, Cincinnati, Ohio
Hill, Norman C , Freeport, Pa
Hinck, C F , Jr , 150 Montclair Ave , Montclair, N J
Hirshleifer, Louis J , 13 Varet St , Brooklyn, N Y
Hitchcock, Frank C , 142 Central Ave , Rahway, N J
Hitchins, Alfred B , cr Ansco Co , Washington St   Binghamton,
N Y
Hochberger, E , 2244 S 50th Ave , Norton Park, Chicago, Ill
Hulett, Edwin B , 4724 Rosehill St , Philadelphia, Pa
Hunt, Orville B , cr Cutter Lab'y Berkeley, Calif
Hutchinson, Charles G , 1 Seaside Ave , Muswell Hill London, N ,
England
Ivarson, Torsten, Virginia, Minn
Jordan, Harry W , cr Solvay Process Co , Syracuse, N Y
Kelley, W W , 5943 Kingsbury Ave , St Louis Mo
Krimmel, M A , 433 East 6th St , Erie, Pa
Kinker, Edward, 3119 Borrman Ave , Avondale, Cincinnati, Ohio
Kinscherf, Carl G , 620 Thurston Ave , Ithaca, N Y
Koelle, Wm G , 5 Section Ave , Hartwell, O
Kuzirian, Simon B , 924 Yale Station New Haven, Conn
Kowalke, O L , Chemical Engineering Bldg , Madison, Wisc
Lewis, George B , 617 Jefferson Ave , Niagara Falls, N Y
Lewis, W B , Cr Sanitarium, Battle Creek, Mich
Lippitt, Thos P , The Dupont, 1717 20th St , N W , Washington, D C
Mason, Jesse H , 182 Sherman St , Canton, Mass
Maury, Robert L , 1024 W 8th St , Wilmington, Del
McAdams, W H , 309 North Broadway, Lexington, Ky
McKay, Robert J , 2616 Hilgard Ave , Berkeky, Calif
Meyer, Emanuel M , 2530 Bell Place, Cincinnati, Ohio
Meyers, Herbert H , 2640 Race St , Denver, Colo
Miller, Walter, 161 Jaques St , Elizabeth, N J
Molton, Blair, 819 Madison St , Evanston, Ill
Montgomery, F J , 1229 Buena Vista St , N S , Pittsburgh, Pa
Musselman, Amos S , 1203 Madison Ave , Baltimore, Md
Nathan, Albert F , Liberty Tower, 55 Liberty St , New York City
Neun, Dora E (Miss), 106 Morningside Drive, New York City
Page, Wm B , Bureau of Soils, Washington, D C
Peter, Arnold H , 2508 Broadway, New York City
Petersen, A H , 64 South Broadway, Akron, Ohio

Pickett, O. A., Box 237, Chapel Hill, No. Car.
Rae, William N., Gov't. Technical Schools, Colombo, Ceylon.
Raymund, Bernard, 215 West 10th Ave., Columbus, Ohio.
Rees, Orton T., 1107 Arch St., Topeka, Kans.
Revel, John W., Gladstone Hotel, Chicago, Ill.
Rhodes, Frederick H., Nanaimo, B. C., Canada.
Roth, George B., 1812 G St., N. W., Washington, D. C.
Saladin, Harry J., 679 Field Ave., Detroit, Mich.
Sawyer, Howard M., 30 Wyman St., West Medford, Mass.
Schener, Elmer, cr. The O. Hommel Co., Pittsburg, Pa.
Schragenheim, E., cr. Thos. Harbauer Co., Toledo, Ohio.
Scott, George, cr. Sherwin Williams Co. of Canada, Ltd., Montreal, Canada.
Simon, Morris, American Oilfields Co., Fellows, Calif.
Smith, Charles V., Box 41, Morse Hall, Cornell Univ., Ithaca, N. Y.
Sneed, M. Cannon, 827 Maple Ave., Newport, Ky.
Somers, Francis P., 439 S. Chicago Ave., Kankakee, Ill.
Stammeler, George F., 505 Luzerne St., Johnstown, Pa.
Steele, Alma (Miss), 303 College Ave., Columbia, Mo.
Stewart, Henry V., Hygienic Laboratory, 25th and E Sts., N. W., Washington, D. C.
Stone, Edward C., 40 Allen Place, Hartford, Conn.
Straw, Walter A., 907 S. 6th St., Champaign, Ill.
Swan, Guy C., Box 422, San Francisco, Calif.
Swenholt, John, Curtice Bros. Preserving Co., Rochester, N. Y.
Taylor, Clifton, Clay & Allison St., Cincinnati, Ohio.
Teeters, W. R., 827 Maple Ave., Newport, Ky.
Thompson, E. D., Walton, N. Y.
Transue, Victor H., Box 633, Port Arthur, Texas.
Turner, William A., 37 Lake Pl., New Haven, Conn.
Voigt, Wm. L., 135 William St., New York City.
Wade, Bruce, Kissam Hall, Nashville, Tenn.
Walters, Edward H., Bureau of Soils, Washington, D. C.
Ward, Fred. W., 292 High Park Ave., Toronto, Ont., Canada.
Weaver, F. R., Box 121, Indiana Harbor, Indiana.
Wemple, H. R., Waverly, Ill.
Wenneis, J. M., 1752 Missouri Ave., St. Louis, Mo.
Whetzel, J. Clyde, Box 204, Lexington, Va.
Wichers, Edward, Chem. Bldg., Univ. of Illinois, Urbana, Ill.
Wiltshire, C. B., 25 University Ave., Battle Creek, Mich.
Worrall, David E., 12 Oxford St., Cambridge, Mass.
Zonker, L. W., Reo Motor Car Co., Lansing, Mich.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

MILWAUKEE SECTION.

At the February meeting of the Section, Professor Victor Lenher, of the University of Wisconsin, gave a very interesting talk on "Recent

Developments in the Chemistry of Gold." The paper dealt with the deposits of gold in nature, their origin, the transportation of gold in solution, and the general chemistry of gold.　　　　C R. McKEE, *Secretary.*

INDIANA SECTION.

On Monday evening, February 9, the Indiana Section was addressed by Dr. Wolfgang Ostwald, of Leipzig, Germany, on "Recent Developments in the Chemistry of Kolloids." The meeting was held in the lecture room of the Science Building of Eli Lilly & Company's plant.
A. B. DAVIS, *Secretary.*

SOUTHERN CALIFORNIA SECTION.

This Section met at the Hollenbeck Café, Thursday evening, February 19, 1914. An informal dinner preceded the meeting. The following program was presented: "The Fixation of Atmospheric Nitrogen," by Dr. Arthur A. Noyes, Massachusetts Institute of Technology. "The Manufacture of Citrus By-Products in Sicily," by Ed. MacKay Chase, United States Bureau of Chemistry. Both subjects were illustrated by slides.　　　　　　　　　　　　WALTER L. JORDAN, *Secretary*

NORTHEASTERN SECTION.

Mr. John J. Elbert, of Worcester, Mass., addressed the Section on February 20 on the following subject: "Fixation of Atmospheric Nitrogen by Means of Boron Compounds."　　　　GRINNELL JONES, *Secretary.*

LOUISIANA SECTION.

The seventy-fourth meeting was held at the Louisiana State Museum, Friday, February 20, 1914. The program of the meeting consisted of an address on "Ceramic Problems," by Paul E. Cox, Ceramic Chemist, Newcomb Pottery.　　　　　　　　J. HEATH LEWIS *Secretary.*

PHILADELPHIA SECTION.

The regular meeting of the Section was held at the Franklin Institute, 15 S. Seventh St., Philadelphia, Penna., on Saturday, February 21, 1914, at 8.15 P.M. An address on "The New Era in Chemistry," illustrated by lantern slides, was delivered by Harry C. Jones, Ph.D., Johns Hopkins University, Baltimore, Md.

The regular meeting of the Section was held at the Engineers' Club, Philadelphia, Pa., March 19, 1914, at 8.15 P.M. Mr. Maximilian Toch, of New York City, gave an illustrated address on "Paint as an Engineering Material."　　　　　　　　C. S. BRINTON, *Secretary.*

CALIFORNIA SECTION.

The seventy-sixth regular meeting of the Section was held at the University of California Club, Saturday, February 21, 1914. The paper

of the evening was on "An Ammonia System of Acids, Bases and Salts," with experiments, by Edward C. Franklin, of Leland Stanford Junior University.   BRYANT S. DRAKE, *Secretary*

RHODE ISLAND SECTION.

The February meeting of the Section was held in Providence, on Thursday evening, February 26. Professor Harlan H. York, Ph.D., of Brown University, spoke on "Some Constructive and Destructive Processes in Plants." Preceding the meeting, a dinner was served in the same room.   NORMAN E HOLT, *Secretary*

MICHIGAN SECTION.

The regular meeting of the Section was held Thursday afternoon, February 26, at 4.30, in the Chemistry Building. Dr. F. E. Bartell spoke on "Some Osmotic Experiments with Porcelain Membranes."
                                                        H. H WILLARD, *Secretary*

DETROIT SECTION.

The meeting of the Detroit chemists was held in the Stevens Building, on Friday, February 27. Mr. Fritz E. Stockelbach, of Frederick K. Stearns & Co., spoke on "Some Organic Syntheses." The speaker was followed by three or four short papers by other members of the Section.
                                                        ROBERT T HARRIS, *Secretary*

NEW HAVEN SECTION.

A meeting was held at the Graduates' Club, on Friday evening, Feb. 27, 1914. Dr. Carl L. Alsberg, Chief of the United States Bureau of Chemistry, addressed the Section upon "Corn Molds and Their Relation to Pellagra."   · GEORGE S. JAMIESON, *Secretary*.

PUGET SOUND SECTION.

The February meeting was held at the Faculty Club House, University of Washington, Saturday, February 28. The paper of the evening was on "Tests on Paving Bricks and Brick Beams," illustrated with the stereopticon, by E. J. Bartells, Denny-Renton Clay and Coal Co.
                                                        RAY W CLOUGH, *Secretary*

OREGON SECTION.

A meeting of the Section was held at the Hazelwood, Portland, Saturday, February 28, at 8.00 P.M. Mr. H. N. Lawrie, Chairman of the Commissioners of the Oregon Bureau of Mines and Geology, addressed the meeting on "The Organization and Activities of the Oregon Bureau of Mines and Geology."   F. A. OLMSTED, *Secretary*.

ROCHESTER SECTION.

The March meeting was held at the University of Rochester, on Monday evening, March 3rd. Mr. W. R. Hurlburt, of the Goldschmidt Thermit Company, spoke on "Thermit—the Theory and Practical Application." The lecture was elaborately illustrated with laboratory experiments, practical welding demonstrations, lantern slides, and motion pictures.

A meeting of the Section was held in Reynold's Laboratory, University of Rochester, on Monday evening, March 16, 1914. Mr. David Coxford spoke on "The Application of Chemistry to the Baking Industry."

WILLIAM H. EARLE, *Secretary.*

PITTSBURGH SECTION

A special meeting of the Section was held in Thaw Hall, University of Pittsburgh, Friday, March 6. Dr. Wolfgang Ostwald, of Leipzig, delivered a series of lectures on "Technical Applications of Colloid Chemistry," under the auspices of the Mellon Institute of Industrial Research, University of Pittsburgh. The Mellon Institute invited the members of the American Chemical Society to attend the entire series of lectures.

C. G. STORM, *Secretary.*

NEW YORK SECTION.

The sixth regular meeting of the session was held in Rumford Hall, 50 E. 41st St., Friday evening, March 6. The following was the program of the evening: Award of the Wm. H. Nichols Medal to M. Gomberg, for his work on Triphenylmethyl. Address by M. Comberg, "The Existence of Free Radicals." Presentation of a bronze bust of Morris Loeb to the Chemists' Club. Acceptance of the bust by Charles F. McKenna, President of the Chemists' Club.

C. M. JOYCE, *Secretary.*

UNIVERSITY OF MISSOURI SECTION.

The 47th regular meeting of the Section was held in the lecture room of the Chemistry Building, Friday, February 20, at 7 o'clock. Dr. P. F. Trowbridge presented a paper on "Studies in Growth," illustrated by lantern slides.

The 48th regular meeting of the Section was held in the Chemistry Building at 7 o'clock, Friday evening, March 6. The following papers were presented by Dr. C. R. Moulton: "Lime Requirement of Soils by Means of the Hydroxides of the Alkaline Earths," and "The Matter and Energy Metabolism of Animals at Constant Weight with Respect to the Active Tissue and the Surface Area."

O. C. SMITH, *Secretary.*

CONNECTICUT VALLEY SECTION.

The regular meeting of the Section was held in Springfield, Saturday afternoon and evening, March 7. The Water Shops and Hill Shops of the United States Armory were visited in the afternoon by forty-three members. Dinner was served at the Highland Hotel, followed by the regular business meeting. The papers for the evening were: (A) "The Progress in Our Knowledge of the Atom," Dr. E. W. Morley. (B) Discussion: "Corrosion of Metal by Water." (C) Discussion: "Use of Electrical Apparatus in the Laboratory." F. P. GILLIGAN, *Secretary.*

ST. LOUIS SECTION.

The regular meeting of the Section was held March 9, 1914, at 8 P.M., at the American Hotel. Mr. Dodge led a discussion on "Fire Risks in Chemical Factories." Dr. Chas. E. Caspari led a discussion on the "Standardization of Weak Solutions." GEORGE LANG, JR., *Secretary.*

LEXINGTON SECTION.

The regular meeting of the Section was held in the College of Agriculture, State University, at 8 P.M., March 11, 1914. Dr. W. R. Fleming, of the Andrews Steel Company, gave an illustrated lecture on "Metallurgy as Applied to Sheet and Pure Iron." G DAVIS BUCKNER, *Secretary.*

CINCINNATI SECTION.

The 190th regular meeting was held at the Ohio Mechanics' Institute, Wednesday, March 11 at 7 30 P.M. The evening was given up to a report on the Spring Meeting. STEPHAN J HAUSER, *Secretary*

WISCONSIN SECTION.

The March meeting of the Section was held in the Chemistry Building at 8 P.M., March 11, 1914. Mr. Harry A. Curtis gave a lecture with demonstrations on "Principles and Methods of Modern Photochemistry." A. E. KOENIG, *Secretary.*

GEORGIA SECTION.

A meeting of the Section was held at De Soto Hotel, Thursday evening, March 12. Matters of business affecting the future policy of the Section were discussed. J. S. BROGDON, *Secretary.*

WASHINGTON SECTION.

The 236th meeting was held at the Cosmos Club, Thursday, March 12, 1914. The following program was presented: R. H. True, "Alcohol and Agriculture in Germany." W. W. Garner, C. W. Bacon and C. L.

Foubert, "Changes that Take Place in the Curing of Cigar-Leaf Tobacco." W. Blair Clark, "A Laboratory Routine Auxiliary to Sugar-Beet Breeding." H. Hasselbring, "Carbohydrate Transformations in Sweet Potatoes during Storage." Illustrated with lantern slides.

ROBERT B. SOSMAN, *Secretary*

SYRACUSE SECTION.

A special meeting of the Section was held Friday, March 13, at 8.15 P.M., in the Syracuse College of Medicine Building. The papers of the evening were: "A Chat on the Development of the Plate," by Mr. E. J. Wall, of Syracuse University. "Electrochemical Indicators, or Instruments for Indicating and also for Continuously Recording the Strength of Solutions from their Electrical Conductivity," by Dr. F. A. Harvey, Syracuse University.

H. B. KIPPER, *Secretary.*

CLEVELAND SECTION.

The regular meeting of the Section was held at the City Club Rooms, Monday evening, March 16. Wm. M. Kinney, of the Universal Portland Cement Co., Pittsburgh, Pa., gave an illustrated lecture on "The Manufacture of Portland Cement."

W. R. KIPPER, *Secretary*

UNIVERSITY OF MICHIGAN SECTION.

The March meeting of the Section was held Tuesday, March 17, in the Chemistry Building. Professor M. Gomberg gave a very interesting review of his work on "The Existence of Free Radicals."

H H. WILLARD, *Secretary*

CHICAGO SECTION.

The March meeting of the Section was held at the Hotel Sherman, March 20, at 8.00 P.M. The subject of the evening was "Wood Preservation," by Clyde H. Teesdale, Forests Products Laboratory, Madison, Wis. The lecture was illustrated by lantern slides and specimens.

D. K. FRENCH, *Secretary.*

NASHVILLE SECTION.

The 24th meeting of the Section was held in Furman Hall of Vanderbilt University, on Friday evening, March 20, 1914, at 8 o'clock. The program included the following papers: "Synthetic Rubber," by Dr. J. T. McGill. "The Enforcement of the National Food and Drugs Act," by Dr. R. W. Balcom.

VICTOR P. LEE, *Secretary*

KANSAS CITY SECTION.

The 100th meeting of the Section was held in the Chemistry Building of the University of Kansas, Lawrence, at 3 P.M., Saturday March 21,

1914.   Dr. William McPherson, of the Ohio State University, gave an illustrated lecture on "European Chemists and Their Laboratories."

Correction: Prof. W. W. Brown also spoke at the February meeting. Subject: "Acid Intoxications of the Body."   W. B. SMITH, *Secretary.*

DECEASED MEMBER.

Barnard, Edith Ethel, Ph.D., instructor in Chemistry at the University of Chicago, March 8, 1914.

Proceedings.

PROCEEDINGS, GENERAL MEETING.

The forty-ninth general meeting of the American Chemical Society was held at Cincinnati, Ohio, Monday, April 6th to Friday, April 10th. The meeting opened with a Council meeting on the evening of April 6th. Tuesday morning the general meeting of the Society was held in the auditorium of the University of Cincinnati and was addressed by the Hon. Frederick S. Spiegel, Mayor of Cincinnati, and by President Charles W. Dabney, of the University of Cincinnati, both welcoming the Society to the city. President T. W. Richards of the American Chemical Society fittingly responded. The Society then held a general meeting, at which the following papers were presented·

"The Chemical Problems of an Active Volcano" (illustrated), by Arthur L. Day.

"The Chemical Fitness of the World for Life," by L. J. Henderson.

"Flame Reactions," by W. D. Bancroft.

"Chemical Reactions at Low Pressures," by Irving Langmuir.

At one o'clock the Society adjourned for an excursion to the Filtration Plant of the Cincinnati Water Works, optional excursions being available to the following plants

Andrews Steel Co , Wiedemann Brewing Co., Old "76" Distilling Co., Frank Tea and Spice Co , Heekin Spice Co., Icy-Hot Bottle Co., Cincinnati's New City Hospital, preceded by car ride through suburbs, The Dolly Varden Chocolate Co., W. T. Wagnets' Sons—Mineral Waters.

In the evening, a complimentary dinner was given to the ladies attending the meeting, followed by a theatre party. At eight o'clock, P.M., a complimentary smoker was held at the Hotel Sinton, with 550 members and guests present. Mementos were given to all those attending, and the smoker will long be remembered, especially for the interesting and witty entertainment provided by the local members, and by talent especially engaged for the occasion.

Divisonal meetings were held on Wednesday morning and all day Thursday at the University of Cincinnati, at which 181 papers were presented, a special symposium on the teaching of organic chemistry being also held by that Division The titles of these papers will appear in the May issue of the *Journal of Industrial and Engineering Chemistry*, and need not be repeated here.

Complimentary lunches were furnished on Wednesday and Thursday. On Wednesday afternoon the members were taken through the works of the Globe Soap Company and Proctor and Gamble, with the following

optional excursions also offered: W. S. Merrell Chemical Co., Lloyd Library & Museum, Fleischmann Distilling Co., American Diamalt Co., Eagle White Lead Co., National Lead Co., Lunkenheimer Co.— Brass Goods, the Zoological Gardens.

On Wednesday evening a Symphony Concert was given complimentary to the members of the Society, and the immense Emery auditorium was filled to hear a concert, under the direction of Ernst Kuhnwald, which has had few superiors in the history of American music:

On Thursday evening, a banquet was enjoyed by the members at the Hotel Sinton, with some 300 present. The banquet was unusual in that especially fine music was furnished by soloists. A decoration particularly worthy of note was an immense American Chemical Society pin in blue and gold flowers.

On Friday, a special train complimentary to the members of the Society took them and their guests to Dayton to visit the works of the National Cash Register Company, where lunch was served to all of those attending, after which the train proceeded to the works of the American Rolling Mills, at Middletown, and from there to Cincinnati. This day's excursion was particularly enjoyed and the works visited were among the most interesting ever opened to the members of the Society.

The meeting closed with the arrival of the members in Cincinnati and will always be remembered by those present. The members and officers of the Cincinnati section put out every effort to insure the comfort and entertainment of their guests, and their hearty good will will never be forgotten by the recipients of their hospitality.

Meetings of all of the divisions of the Society, as well as the India Rubber Section and the Water, Sanitation and Sewage Section were held. Details will appear in the published program, as above stated.

The meeting was the largest spring meeting ever held, in the history of the Society, 658 members and guests being present.

CHARLES L. PARSONS, *Secretary.*

DIRECTORS' MINUTES.

The Directors met at the University of Cincinnati, in Cincinnati, Ohio, at 10.30 o'clock, A.M., Thursday, April 9th, with President Richards in the chair, and Directors Bigelow, Brady, Smith and Parsons present.

The Secretary was directed to send a vote of thanks to the President of the Cincinnati Section, Frederick W. Weissmann; the Secretary, Stephan J. Hauser; the members of the Cincinnati Section; to the Chairmen of the local committees, Mrs. J. W. Ellms, Archibald Campbell, G. Farnham, C. T. P. Fennel, John Uri Lloyd, J. W. Ellms, R. Lord, Lauder W. Jones, F. C. Broeman, F. O. Clements, and through them to the members of their committees; the trustees and President of the University of Cincinnati; the Mayor of Cincinnati; Director Ernst Kuhnwald, Conductor

ſf the Cincinnati Symphony Orchestra; Emil Hermann, violin soloist ɔf this orchestra; to the officials of the various plants which had opened heir works and shown courtesies to the American Chemical Society; to Professor E. B. Remelin for his scientific (?) lecture at the smoker, and to Dr. H. M. Goettsch for his untiring attention to the detail of the meeting.

A letter from Mr. J. J. Miller, Associate editor of Chemical Abstracts, was presented to the Directors pointing out the necessity for further funds and increased space in *Chemical Abstracts*, and it was voted that the editor be authorized to increase the average size of the issue for the year 1914 from 170 to 175 pages, and that $1250 additional be appropriated to *Chemical Abstracts*.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

COUNCIL MINUTES.

The Council of the American Chemical Society met at the Hotel Sinton, Cincinnati, Ohio, on Monday evening, April 6th, at eight o'clock, P.M., with President Richards in the chair, and the following councilors and substitutes present:

R. H. McKee, E. H. S. Bailey, W. D. Bancroft, F. K. Cameron, Alex. Smith, L. C. Drefahl, H. P. Talbot, K. G. Mackenzie (sub.), R. W. Rohde, F. W. Robison, W. D. Bigelow, S. W. Parr, L. W. Jones, Chas. Baskerville, Friend E. Clark, W. E. Henderson, J. I. D. Hinds, H. N. McCoy, W. F. Hillebrand, J. H. Ransom, S. F. Acree, M. X. Sullivan (sub.), J. T. Baker, G. B. Frankforter, W. J. Hale (sub.), W. T. Taggart, A. M. Breckler, P. A. Kober (sub.), Bernhard C. Hesse, A. Campbell, F. R. Eldred, W. F. Montfort, L. A. Touzalin, L. I. Shaw (sub.), Wm. Brady, C. H. Herty, F. N. Smalley, S. S. Voorhees (sub.), I. K. Phelps (sub.), G. P. Adamson, W. D. Richardson, H. E. Howe (sub.), D. K. French, A. C. Langmuir, E. W. Washburn, E. Bartow, J. Steiglitz, W. A. Noyes, J. Kendall (sub.), F. B. Allan, and A. H. Sabin (sub.)

A change in the By-laws of the Fertilizer Division by which Article 5 of that Division was changed to read as follows:

"The chairman shall, with the advice and approval of the executive committee, appoint from time to time standing committees of the Division to consider, conduct and report upon such special matters as may be delegated to them The following committees shall be appointed at the annual meeting, or as soon thereafter as may be expedient: *a*. Committe on Fertilizer Legislation. *b*. Committee on Research and Methods of Analysis."

was approved by the Council.

The invitation of the Louisiana Section to hold the spring meeting of 1915 in New Orleans was accepted and the Secretary was directed to

arrange for the exact date with the officers of that section and to thank them.

A communication was presented to the Council from the secretary of the Committee on Organization and Membership of the American Association for the Advancement of Science, stating that the American Association had arranged to have, every four years, a meeting in one of our larger cities in the hopes that the American Chemical Society and other societies not now regularly affiliated with the association might be induced to meet with them at these four-year periods. It was voted that the Secretary be instructed to reply that the sentiment of the Council was entirely favorable to the proposed plan, and to state that it is the opinion of the Council that the American Chemical Society will hold its annual meeting in 1916 with the American Association for the Advancement of Science at the place selected, convocation week, December-January, 1916–1917.

A communication was received from the President of the Cotton Products Analysts, asking by what arrangement their Society could become a section or division of the American Chemical Society. After some discussion it was voted that the Cotton Products Analysts be invited to become a section of the American Chemical Society under the usual conditions covering sections of the Society, the same to be explained in detail to the officers of the Cotton Products Analysts by the Secretary.

Committee reports were then presented to the Council through the President, as required by the Constitution. The reports of the following committees were accepted and placed on file: on Patent and Related Legislation, on Standard Methods of Water and Sewage Analysis, on Paper, the Perkin Medal Committee, on Membership, on Exchanges, on the Quality of Reagents, on Endowment, on Occupational Diseases, and on Notation of Physical Chemistry. The report of the Committee on Inorganic Chemical Nomenclature brought out extended discussion. It was voted by a large majority (44 to 1) that the Council of the American Chemical Society are in favor of the use of "beryllium" rather than "glucinum" and that this preference be transmitted by the Secretary and the Society's delegates to the International Council of Chemical Societies. It was voted also by a large majority (32 to 2) that the Council favor the name "columbium" rather than "niobium" and it was directed that the Secretary and our representatives on the International Council transmit the request to the International Council that they reconsider their action in favor of "niobium," especially in consideration of the following statement of F. W. Clarke, chairman of the International Committee on Atomic Weights:

At a meeting of the Council of the International Association of Chemical Societies in Brussels, last September, a committee on inorganic nomenclature, among other

ecommendations endorsed the name and symbol "niobium" and "Nb," for the ele ment which was originally named columbium As this recommendation is historically erroneous, a brief statement of the facts appears to be desirable

In 1801, Hatchett, an English chemist, analyzed a strange American mineral, and in it found a new metallic acid, the oxide of an element which he named columbium A year later, Ekeberg, in Sweden, analyzed a similar mineral from Finland, and discovered another element, which he called tantalum Wollaston, in 1809 undertook a new investigation of these elements, and concluded that they were identical, a conclusion which, if it were true, would have involved the rejection of the later name and the retention of the earlier columbium The accepted rules of scientific nomenclature make this point clear

For more than forty years after Hatchett's discovery both names were in current use, for although Wollaston s views were accepted by many chemists, there were others unconvinced In 1844, however, Heinrich Rose, after an elaborate study of columbite and tantalite from many localities, announced the discovery of two new elements in them, niobium and pelopium The latter supposed element was afterwards found to be non-existent, but the niobium was merely the old columbium under a new name That name in some mysterious manner was substituted by the German chemists for the original, appropriate name, and has been in general use in Europe ever since In America, the name columbium has been generally preferred, and was formally endorsed by the Chemical Section of the American Association for the Advancement of Science more than twenty years ago In England, also, columbium is much used, as for example, in Roscoe and Schorlemmer s *Treatise on Chemistry*, Thorpe s *Dictionary of Applied Chemistry*, and the new edition of the *Encyclopedia Britannica*

The foundation of Rose's error seems to have been an uncritical acceptance of Wollaston's views, for he speaks of all the minerals he studied as tantalite He also, at least in his original memoir, claims that the atomic weight of niobium is greater than that of tantalum, and here he was obviously wrong

In short, the name columbium has more than forty years' priority, and during that interval was accepted by many chemists, and was more or less in current use To employ the name niobium is not only unhistorical, but is also unfair to the original discoverer, meaningless, and without any justification whatever Furthermore, it injures the splendid reputation of Rose, for it perpetuates and emphasizes one of his few errors The recommendation of the committee above mentioned should not be accepted, for it is opposed to the established rules of priority

It was voted that the Council disapproves of the recommendation K" of the International Association's Committee in Organic Nomenclature in reference to the suffixes -o, -a, -i, -e, -on, -an, in, and -en, to indicate the valencies from 1 to 8. It was voted to refer the remainder of this report back to the committee to report directly to the International Council, and the Secretary was directed to place the whole report on file.

The reports of the Finance Committee and the Supervisory Committee on Methods of Analysis were received and ordered printed

Report of the Finance Committee.

To the Members of the American Chemical Society

In accordance with the requirements of the Constitution of the Society, your Finance Committee begs to submit the following report for the year ending November 30, 1913

All bills presented during the year have been examined and approved by the Committee before payment by the Treasurer

Acting under the authority of the Committee, Messrs J Yalden & Co , certified public accountants, have audited the accounts of the Treasurer, and report as follows·
"As per instructions received, we have audited the books and accounts of your Treasurer, Dr A P Hallock, for the year ending December 1, 1913, and beg to report that we have found the same correctly kept and all payments made on the authority of duly approved vouchers

"The cash on hand, as shown by the books, is in accord with that as shown by the banks, as follows

Farmers Loan and Trust	$5,478 04
First National Bank, Yonkers	2,901 73
	$8,379 77

"We also notice there is a fund known as the Morris Loeb Endowment Fund' which has been created for a special purpose and is on deposit, and amounts to $25,000 00

"The securities owned by the Society, we have examined and find them to be as stated on your Balance Sheet We are also informed that there are no liabilities existing, with the possible exception of the Life Membership Fund "

The statement of the Treasurer's accounts together with the Balance Sheet are attached (See January Proceedings)

Respectfully submitted
E G Love,
G C Stone
A W Hill
Finance Committee

Report of the Supervisory Committee on Methods of Analysis.

In accordance with the provision of the Constitution relating to Standing Committees, I submit to you, for transmission to the Council my report as Chairman of the Supervisory Committee on Methods of Analysis covering the period since February 27, 1913, the date of my last report

In general it will be seen that little activity has been manifested by some of the committees engaged in the study of analytical methods, and no reports of a final character have been made The membership of the several committees has undergone little change

I   COMMITTEES OF THE GENERAL SOCIETY

1   Committee on Revision of Methods of Coal Sampling and Analysis

A joint committee representing the American Chemical Society and the American Society for Testing Materials A preliminary report from this committee was published in the *Journal of Industrial and Engineering Chemistry*, 1913, page 517, and it was made the basis for discussion at the Rochester meeting in September, 1913 The committee has been at work on a modified report which will be discussed at the Cincinnati meeting in April next, and also at the June meeting of the American Society for Testing Materials

2   Committee on Methods of Analysis of Potable Waters and Sewage

As mentioned in my last report, this committee is working in conjunction with a similar committee of the American Public Health Assoc ation Topics have been assigned to members of the two committees and the methods published in 1912, by the American Public Health Association will be tested and revised if necessary A progress report will be presented at the Cincinnati meeting

II   DIVISIONAL COMMITTEES

A Division of Industrial Chemists and Chemical Engineers

1   Committee on Standard Specifications and Methods of Analysis

In September last, Mr. H. J. Skinner, Chairman, resigned. At the date of this report his place has not been filled nor has a new chairman been appointed. Mr. Skinner on retiring presented to the Division a report, from which as well as from later information supplied by Mr. Skinner and the Chairman of the Division, it appears that:

(*a*) A new subcommittee was appointed to consider the whole subject of heavy mineral acids, by combination of the several committees formerly in charge of a single material each, but as yet no report has been rendered.

(*b*) The three subcommittees on Caustic, Soda Ash and Bleaching Powder have been combined in one subcommittee on Bleach and Alkali.

(*c*) The subcommittee on alloy analysis has accumulated sufficient data to enable it to formulate a standard method for the determination of copper in refined copper and also in copper containing the usual impurities. When the method has been formulated samples of copper will be distributed for coöperative analysis The membership of this subcommittee is: W. B Price, Chairman, George L Heath, Gilbert Rigg, Bruno Woiciechowski, and Alden Merrill.

(*d*) No reports have been rendered by any subcommittee

2. Committee on Soap and Soap Products

No progress has been made, owing to the inactivity of subcommittees

B Division of Fertilizer Chemists

1. Committee on Potash

The progress report presented at the Milwaukee meeting in March, 1913, has been published in the *Journal of Industrial and Engineering Chemistry*, 1913, page 431. No new work is contemplated at present.

2. Committee on Phosphoric Acid.

At the Rochester meeting in September, 1913, it was decided to place the work of the various subcommittees on analysis in the hands of the Executive Committee of the Division for approval The chairman will submit to the Executive Committee at the Cincinnati meeting of the Division a résumé of work done, with recommendations for future work. A report, supplementary to that appearing in the *Journal of Industrial and Engineering Chemistry*, **3**, 118, is to be found in the same Journal, **5**, 956.

3. Committee on Nitrogen.

The Committee on Nitrogen has in hand the preparation of a suitable sample of commercial nitrate of soda for coöperative work. No report of progress has been made during the year.

4. Committee on Phosphate Rock.

A report of progress from the committee was published in the *Journal of Industrial and Engineering Chemistry*, **5**, page 957.

C. Division of Pharmaceutical Chemists.

Committee on Quantitative Methods of Analysis.

No reports have been printed during the year, but a progress report will be presented at the Cincinnati meeting. The work now in hand has been divided into three sections, each of which will receive special investigation by a member of the committee. The subjects are: The quantitative estimation of santonin and of quinine and strychnine, particularly in pharmaceutical preparations, and of mercuric iodide, in pills and tablets.

D. Section of India Rubber Chemists.

Committee on Analysis of Rubber and Rubber Products.

This committee has worked continuously on a procedure for analysis Preliminary reports have been submitted to the Section and another report will be made at the Cincinnati meeting in April.

W. F. HILLEBRAND, *Chairman, Supervisory Committee on Methods of Analysis.*

The Report of the Committee on Business Management was then received, and after a short discussion it was voted that the committee

have printed and sent to the individual members of the Council at t
expense of the Society their report, together with such arguments f
and against the action recommended as it may see fit, that the Councild
consult their sections as they may see fit, that this report be discuss
at an annual meeting, finally a letter ballot on each individual questi
be taken, and that in the meantime the report be laid on the table.
was further voted that if the report and arguments reach the sectid
before May 15th, the report shall be considered at the Montreal meetin
if later than May 15th, at the annual meeting of 1916.

The Council then adjourned.

CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15, 1914.

Angier, F. J., Mt. Royal Station, Baltimore, Md.
Bayless, Raymond Theodore, 194 Helen Ave., Detroit, Mich.
Betz, C. E., 303 South Ave., Wilkinsburg, Pa.
Black, T. S., Cudahy Refining Co., Chicago, Ill.
Blanc, Charles, 362 E. Buchtel Ave., Akron, Ohio.
Blaut, Samuel J., 331 East 51st St., New York City.
Bloom, Oscar T., 7211 Stewart Ave., Chicago, Ill.
Bogart, James H., Detroit Insulated Wire Co., Detroit, Mich.
Burn, Harry, 1319 ... Ave., Birmingham, Ala.
Carr, R. H., 24 ... St., LaFayette, Indiana.
Carter, H. W., ...one Tire and Rubber Co., Akron, Ohio.
Chamberlain, Will. Hepburn, 1124 East Capitol St., Washington, D.
Chapman, Cloyd M., 37 Wall St., New York City.
Childs, David H., 261 Huntington Ave., Buffalo, New York.
Collitt, Bernard, 37 South Park, Lincoln, England.
Comstock, Daniel F., Inst. of Technology, Boston, Mass.
Cooper, Albert B., 56 Ave., Lachine, Quebec, Canada.
Cox, Frank, 312 Maple Ave., Danville, Ky.
Cross, Wilbur N., 6600 Yale Ave., Chicago, Ill.
Deitemeier, Wilhelmine, 2519 Homestead Place, Cincinnati, Ohio.
Dejonge, Emil, Fitchburg, Mass.
Eicher, B. L., 518 East 42nd St., Chicago, Ill.
Emley, Warren E., Bureau of Standards, Pittsburgh, Pa.
Fenger, Frederic, 3932 Lake Park Ave., Chicago, Ill.
Frank, Leslie C., U. S. Public Health Service, Washington, D. C.
Frederiksen, F. M., 47 South Ave., Ithaca, New York.
Ginsburg, S. M., 66 Munroe St., Roxbury, Mass.
Grimshaw, Albert H., 289 Purchase St., New Bedford, Mass.
Goebel, Lee H., 1281 3rd Ave., E., Cedar Rapids, Iowa.
Goldstein, Joseph, 1501 North Hoyne Ave., Chicago, Ill.
Graham, William, 611 Bailey Farrell Bldg., Pittsburgh, Pa.
Gross, Edward L., 1112 West 37th Street, Chicago, Ill.
Gross, Nels, 759 Pensacola Ave., Chicago, Ill.
Harrison, John William, Trinity College, Hartford, Conn.
Hess, J. Raymond, 222 East 8th St., Topeka, Kan.
Hiller, Fred. L., 571 Linden Ave., York, Pa.
Hovey, R. W., 250 Sherbrooke St., W., Montreal, Quebec, Canada.

Huestis, James D., Fonda, New York.
Hume, Robert F., 229 South 2nd St., Duquesne, Pa.
Hutshing, Edwin E., 1013 Green Bldg., Seattle, Wash.
Johnson, Arthur K., Andover, Mass.
Katz, Louis, Food and Drug Lab., 641 Washington St., New York City.
Kelly, Ed., 76 Court St., Brooklyn, New York.
Kelly, William, Transportation Bldg., Montreal, P. Q., Canada.
Kuhre, Kenneth D., Sandy, Utah.
Lloyd, H. E. care Barrett Mfg. Co., 2900 So. Sacramento Ave., Chicago, Ill.
Luck, Julius, A. W., 2433 Telegraph Ave., Berkeley, Cal.
Lusskin, Abraham, 1015 E. 156th Street, New York City.
Marszalek, John A., 2838 Washington Blvd., Chicago, Ill
McEwen, Lyman, O'Brien Mine, Cobalt, Ontario, Canada.
McIntosh, James, Diamond State Fibre Co., Bridgeport, Montgomery County, Pa.
McLachlin, A. F., 115 Ross St., St. Thomas, Ontario, Canada.
Méndez, Joaquin, Clarkson College, Potsdam, New York.
Merica, Paul D., Chemical Bldg., Urbana, Ill.
Merry, George B., Stillwater, Oklahoma.
Mitchell, Roy C., 430 W. Symmes St., Norman, Oklahoma.
Monroe, Kenneth Potter, Norman, Oklahoma.
Morrissey, John P., St. Xavier College, Cincinnati, Ohio
Nelson, Hubert E., 3438 Polk St., Chicago, Ill.
Neuffer, Leonora, 315 Patterson St., Lockland, Cincinnati, Ohio
Parks, L. R., State College, Pa.
Rowell, Harry E., 629 Terrace Place, Schenectady, New York.
Savage, John W., 3890 Grant Blvd., Pittsburgh, Pa.
Saxon, Gordon J., 5314 Spruce St., Philadelphia, Pa.
Scherrer, Peter, 2814 Vine St., Cincinnati, Ohio.
Shakman, James G., 5013 Grand Blvd., Chicago, Ill.
Slater, Henry Byron, Riverside, California.
Smith, Frank B., Linden House, Bayonne, N. J.
Smootz, John P., Oak Union, Ohio State Univ., Columbus, Ohio.
Stockmayer, Dr. Hugo, 124 Prospect Place, Rutherford, N. J.
Streeter, H. W., 2012 Clarion Ave., Cincinnati, Ohio.
Suer, Werner John, 314 W. McMillan St., Cincinnati, Ohio.
Sykes, Roy A., 108 Howe Ave., Passaic, N. J.
Tyson, Harry E., Weatherly, Pa.
Waring, F. Hohman, 2211 McGregor Place, Cincinnati, Ohio.
Watts, Hugh F., 923 Pearl St., Boulder, Colorado.
West, Augustus P., University of the Philippines, Manila, P. I.
Wickizer, H., 1214 N. Main St., Los Angeles, Cal.
Williams, Seward, care Bauer and Black, 25th and Dearborn Sts., Chicago, Ill.
Williams, W. E., 4433 Lake Park Ave., Chicago, Ill.
Wolf, Fred. L., Ohio Brass Co., Mansfield, Ohio.
Wollner, Leo, 1537 Clybourn Ave., Chicago, Ill.
Wright, Neil, Highland and Kinsey Aves., Cincinnati, Ohio.

CORPORATION MEMBERS.

Consolidation Coal Co., Fairmont, West Virginia.
Mallinckrodt Chemical Works, St. Louis, Mo.

MEETINGS OF THE SECTIONS.

WESTERN NEW YORK.

The January meeting was held in the Lecture Hall of Canisius College, Buffalo, N. Y., on January 13, 1914. Mr. H. E. Howe, of the Bausch & Lomb Optical Co., Rochester, N. Y., gave an illustrated lecture on the manufacture of optical glass and also gave a lantern demonstration of the projection of spectra. The meeting then adjourned. After the formal session of the meeting was over, the members were entertained by Father Ahern and his colleagues.

A meeting of the section was held on Friday, March 20th at 8.30 at the University of Buffalo, Buffalo, New York. The following papers were presented: "Accident Prevention," by Walter Wallace. "Treatment of Minor Injuries by the Chemist," by Charles E. Taylor. "First Aid ' by W. Lewis Wilson. Previous to the meeting an informal dinner was served.   WALTER WALLACE *Secretary*

UNIVERSITY OF ILLINOIS SECTION.

The regular 519 Ave., Birming...tion was held on January 14th. Dr. Wolf, W., 24 ... St ... the University of Leipzig, lectured on the subject "lain, Will Imistry."

The Fe, Clay meeting was held February 24th and was addressed by Mr. J. R. Powell, Chief Chemist of the Armour and Company Soap Works, Chicago. Mr. Powell's subject was "Perfumes."

On March 18th a joint meeting of the Section with the Illinois Chapter of Sigma Xi was addressed by Professor S. W. Parr on "Some Western Fuel Problems."   D. F. McFARLAND, *Secretary*

OREGON SECTION.

The 10th regular meeting was held at The Hazelwood, Portland, Saturday evening, January 17th, preceded by the usual dinner. A paper was presented by Mr. A. A. Wagner on "The Electron Conception of Valence Oxidation and Reduction."

The 11th regular meeting of the Oregon Section was held at The Hazelwood, Portland, Saturday evening, February 28th, preceded by a dinner. It was voted to accept the invitation of the Puget Sound Section and join with them in a meeting of all the coast sections to be held in Seattle in connection with the annual meeting of the Pacific Association of Scientific Societies in May. A paper was presented by H. N. Lawrie, chairman of the Board of Commissioners of the Oregon Bureau of Mines and Geology on "The Organization and Activities of the Oregon Bureau of Mines and Geology."

The 12th regular meeting of the Section was held at The Hazelwood,

ortland, Saturday evening, March 28th. The following papers were
esented: "Arsenates of Lead and their Insecticidal Properties,"
7 H. V. Tartar and R. H. Robinson. "Electric Steel Furnace Work,"
⸱ A. E. Green.   F A OLMSTED *Secretary*

WASHINGTON SECTION.

There was a joint meeting with the Washington Academy of Sciences
Monday, March 16th, at 8.30 P.M., at the Cosmos Club. The following
dress was given: "The Chemistry of Colloids," by Dr. Wolfgang
.wald, of the University of Leipsic.

The 237th meeting was held at the Cosmos Club, Thursday, April
914. The program consisted of the following papers ' H. S. Washing
, "The Distribution of the Chemical Elements in the Earth's Crust '"
P. Dewey, "The Pyrometer in the Assay Muffle " W. O Emery
and S. Palkin, "The Estimation of Antipyrin." R. E. Lee, "The Guil-
laume Apparatus for the Distillation and Rectification of Alcohol."

ROBERT B SOSMAN, *Secre ⸱y*

SOUTHERN CALIFORNIA SECTION.

The regular March meeting of this Section was held at the Hollenbeck
Café, Thursday evening, March 'a..e, C.....Annainformal dinner at six
o'clock preceded the meetir⸱ St., Chicago, Ill.   presented:
"The Slater Process of Extracting Copper ᵗrᵉ· and, Cincinnati, Ol ores," Dr.
Harry W. Morse. "Some Interesting Non-technical ᵣₒ.ₑᵥ York of German
Industry," Mr. Walter A Schmidt.

The regular April meeting of the Section was held at the Hollenbeck
Café, Thursday evening, April 16, 1914 An informal dinner preceded
the meeting. The following program was presented "Some Phases
of German Chemical Industry, Including the Manufacture of Dyestuffs,"
Dr. Wilhelm Hirschkind. "The Manufacture of Automobile Tires,"
Mr. S. P. Thacher.   WALTER L JORDAN, *Secretary*

PITTSBURGH SECTION

The 106th regular meeting of the Section was held at the Central Turn
Verein, Pittsburgh, Pa., Thursday, March 19, 1914. A paper on "A
Definition of Plasticity" was read by Mr. W. E. Emley, Ch.E., National
Bureau of Standards, Pittsburgh, Pa. The meeting was a smoker and
gave the members of the Section an opportunity of becoming better
acquainted. The entertainment committee provided unusual entertain-
ment features and refreshments.

The 107th regular meeting of the Pittsburgh Section of the America
Chemical Society was held at the University of Pittsburgh, Wednesdr
April 15, 1914. Professor C. W. Bennett, of Cornell University, lectu
on "The Fixation of Nitrogen." This paper was of special inte
Professor Bennett has first-hand knowledge of the problem, having
actively engaged in the study of cyanamid in this connection.

C. G STORM, *Secr·*

UNIVERSITY OF MISSOURI SECTION.

On Friday evening, March 20th, the 48th regular meeting of the Section was held. Dr. C. R. Moulton presented a paper on "The Matter and Energy Metabolism of Animals at Constant Weight with Respect to the Active Tissue and the Surface Area."

The 49th regular meeting of the Section was held in the lecture room of the Chemistry Building, Friday evening, April 3rd. Mr. E. C. Pegg, of the Department of Forestry gave an illustrated lecture on "The Manufacture of Wood Pulp and Paper." After the illustrated lecture, Mr. Preston Thomson, Superintendent of the Forest Products Chemical Company, of Memphis, Tenn., gave a talk on "Dry Distillation of Hard Wood."

O C SMITH, *Secretary*

MINNESOTA SECTION.

A regular meeting was held Friday, March 20th, at 8 P.M., in the chemical laboratory of the University of Minnesota. Dr. J. F. McLendon, of the Dept. of Physiology spoke on "Some Applications of Physical Chemistry to Certain Biological Problems."

W H HUNTER *Secretary*

LOUISIANA SECTION.

The 74th meeting was held at the Richardson Chemical Building, Friday, March 20, 1914. The program of meeting was: "Observations upon Surface Tension—Experimental," by Dr. Ralph Hopkins. "Histidin: Preparation and Properties," by Dr. R. G. Meyers.

J HEATH LEWIS, *Secretary-Treasurer*

CORNELL SECTION.

March meeting was held Monday evening, March 23, 1914, in Morse Hall. Professor Heinrich Ries talked on "Underground Water Supply."

The April meeting was held Monday evening, April 20, 1914, in Morse Hall.

.. H. \ Norwood of the Taylor Instrument Companies, Rochester gave an illustrated talk on "The Mercurial Thermometer and its Adaptation to Industrial Arts."

O. R OVERMAN, *Secretary*

DETROIT SECTION.

The meeting on March 27th was a social evening to which ladies were invited. There were three non-technical short talks given by members of the society. The rest of the evening was devoted to music, social intercourse and refreshments.

ROBERT T. HARRIS, *Secretary*

EASTERN NEW YORK SECTION.

The March meeting was held in the Chemical Lecture Room at Union College, Schenectady, on Friday evening, March 27th.

Dr. F. Jewett Moore, Ph.D., Professor of Organic Chemistry in the Massachusetts Institute of Technology, spoke on "Modern Syntheses of Compounds of the Tannin Class."

W. C. ARNOLD, *Secretary*